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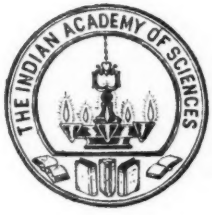

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ON m CONSECUTIVE INTEGERS—II*

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(Communicated by Prof. B. S. Madhava Rao)

I. Introduction

Let $f(y)$ be a polynomial with integral coefficients, and $P(m)$ denote the product of any set of m consecutive integers; *i.e.*,

$$P(m) = n(n+1)\cdots(n+m-1).$$

Then the question whether the equation

$$P(m) = f(y) \tag{1}$$

is possible, and, if so, whether it has got an infinite number of solutions, is a very interesting and at the same time, very difficult one. Unless the equation is an identity, it is probable that it has got, if at all, only a finite number of solutions. When $f(y)$ is irreducible, the solution is immediate. In that case, let p be the smallest prime which does not divide $f(y)$ for any y.† Then, since $P(m)$ is divisible by $m!$, the equation (1) is impossible when $m \geqslant p$. For example, let us consider $f(y) = y^2+1$. In this case, y^2+1 is not divisible by 3. So when $m \geqslant 3$,

$$P(m) \neq y^2+1.$$

Further, if $n(n+1) = y^2+1$, then, when $n \geqslant 2$, $n+1 > y > n$.

So we get that, when $m \geqslant 2$ and $n \geqslant 2$, the equation

$$P(m) = y^2+1$$

has no solution.

It is easy to construct any number of $f(y)$'s for which the equation (1) has no solution. It is, though trivial, interesting to observe that, if the absolute term in $f(y)$ is odd and the sum of the coefficients of the rest of the terms is even, then the above equation is impossible. One particular case of this is that

$$P(m) = (y^r \pm 1)/(y \pm 1)$$

has no solution, when r is odd.

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* This is a slightly modified form of a portion of my Thesis for the degree of M.Sc. in the Madras University. Theorem C is not in the Thesis.

† Frobenius has proved that $f(y)$ has got an infinite number of primes which do not divide it.

In this paper, I consider only the case when $f(y) = y^r$. The problem is whether the product of m consecutive integers can be a perfect power. For known results about this problem, reference may be made to pages 679, 680 in Dickson's *History of the Theory of Numbers*, Vol. II.* Though it is reasonable to conjecture that P (m) cannot be a perfect power in any case, the proof seems to be difficult. In this paper, I prove the following results:

THEOREM A: When $2 \leqslant m \leqslant 16$ and $r \geqslant (m+3)/2$, the equation

$$\mathrm{P}(m) = y^r \tag{2}$$

is impossible.

THEOREM B: The equation (2) has, if at all, only a finite number of solutions, provided $r \geqslant 3$.

THEOREM C: There is a number $c = c(m)$ such that, when $r > c$, the equation (2) has no solution.

II. Notation and Lemmas

$g(n) = \theta\{f(n)\}$ means that

$$|g(n)| \leqslant |f(n)|$$

$n + t$ denotes a number among $n, n+1, \cdots, n+m-1$, which is prime to all the rest (if any).

Lemma (1): When $m \leqslant 16$, in every set of m consecutive integers, there is at least one which is prime to all the rest in the set.

This is proved in Paper I with the same title.

Lemma (2): If $n(n+1)\cdots(n+m-1) = y^r$ and $n+t$ exists, then

$$n + t \geqslant (m/2)^r.$$

Since $n \leqslant n+t \leqslant n+m-1$, if $p \leqslant m/2$, either $n+t-p$ or $n+t+p$ lies in the interval $(n, n+m-1)$. But $n+t$ is prime to all the rest of the numbers in the above interval. So $n+t$ is divisible by no prime $\leqslant m/2$. But $n+t$ should be an rth power.

Hence

$$n + t \geqslant (m/2)^r.$$

Lemma (3): If $p^b \mid (p^a + \mathrm{N})$,

then

(1) $p^b \mid \mathrm{N}$, when $b \leqslant a$,

(2) $p^a \mid \mathrm{N}$, when $b > a$.

It is obvious.

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* See a paper by Paul Erdes in a recent issue of *I.L.M.S.*, Vol. 14, Part 3.

Lemma (4): If $n(n+1)\cdots(n+m-1) = y^r$, $^*p^\psi \| n$, and $\psi \geqslant m$, then

$$l \geqslant r - m,$$

where $$\psi = rs + l,\ o \leqslant l < r.$$

Since $\psi \geqslant m$, k the highest power of p which divides $(n+1)(n+2)\cdots(n+m-1)$

$$\leqslant [(m-1)/p] + [(m-1)/p^2] + \cdots \leqslant m - 1.$$

Since $n(n+1)\cdots(n+m-1) = y^r$, $k + \psi \equiv 0 \pmod{r}$.

So $l + k \equiv 0 \pmod{r}$. But $k \leqslant m - 1$.

Hence $l \geqslant r - m$.

Lemma (5): If $n(n+1)\cdots(n+m-1) = y^r$ and $p^\psi \| n$, then we can find one $a \leqslant m$, such that either $p^{\psi - a} = x^r$, or, $p^\psi . p^a = x^r$.

If $\psi \leqslant m$, then $a = \psi$ and there is nothing to prove. If $\psi > m$, then from lemma (4),

$$\psi = rs + l, \text{ where } l \geqslant r - m.$$

So $$\psi = (s+1)r - a, \text{ where } a \leqslant m.$$

Hence $$p^a \cdot p^\psi = x^r.$$

Lemma (6): If $n(n+1)\cdots(n+m-1) = y^r$ and $p^\psi \| (n+1)$, then we can find one $a \leqslant m$, such that either $p^{\psi - a} = x^r$ or $p^{\psi + a} = x^r$.

Under the hypothesis of lemma (6), the lemma (5) can be proved. Hence the present lemma easily follows.

III. Theorems

Hypothesis A: There is at least one integer $n + t$ among n, $n+1$, $\cdots$, $n + m - 1$, which is prime to all the rest in the above set.

THEOREM I: If Hypothesis A is true, then, when $r \geqslant m + 1$ and $m \geqslant 4$,

$$n(n+1)\cdots(n+m-1) \neq y^r.$$

If possible, let

$$n(n+1)\cdots(n+m-1) = y^r.$$

Since $n + t$ is prime to $n(n+1)\cdots(n+t-1)(n+t+1)\cdots(n+m-1)$

$$n + t = x^r, \tag{3}$$

and $$n\cdots(n+t-1)(n+t-1)\cdots(n+m-1) = z^r. \tag{4}$$

---

* $p^\psi \| n$ means that $p^\psi \mid n$ and $p^{\psi+1}$ does not divide n.

Therefore z is prime to x. (5)

From (4), (3), we get that

$$z^r = (x^r - t) \cdots (x^r - 1)\,(x^r + 1) \cdots (x^r - t + m - 1).$$

So

$$r \log z = (m-1)\, r \log x + \log\,(1 - t/x^r) + \cdots + \log\,\{1 + (m - 1 - t)/x^r\}$$

$$= (m-1)\, r \log x + \frac{A_1}{x^r} + \frac{A_2}{2 \cdot x^{2r}} + \cdots\cdots, \tag{6}$$

where

$$|A_s| \leqslant m^{s+1}/(s+1). \tag{7}$$

From lemma (2), $x \geqslant m/2$.

So

$$1/x^r \leqslant (2/m)^r \leqslant (2/4)^5 = 1/32. \tag{8}$$

$$m/x^r \leqslant m/x^5 \leqslant 2/x^4 \leqslant 1/8 \tag{9}$$

$$m^2/x^r \leqslant m^2/x^5 \leqslant 2^5/m^3 \leqslant \tfrac{1}{2} \tag{10}$$

From these, we get that

$$\left| \frac{A_1}{x^r} + \frac{A_2}{2 \cdot x^{2r}} + \cdots \right| \leqslant \frac{m^2}{3x^r} + \frac{m^3}{6x^{2r}} + \cdots$$

$$\leqslant \frac{m^2}{x^r}\left\{\frac{1}{2} + \frac{1}{6} \cdot \frac{m}{x^r} + \frac{1}{12} \cdot \frac{m^2}{x^{2r}} + \cdots\right\}$$

$$\leqslant \frac{m^2}{x^r}\left\{\frac{1}{2} + \frac{1}{3} \cdot \frac{m}{x^r}\right\} \leqslant \frac{3}{4} \cdot \frac{m^2}{x^r}. \tag{11}$$

Again

$$\left| e^{\theta\,[3m^2/(4rx^r)]} - 1 \right| = \theta\left(\frac{3}{4} \cdot \frac{m^2}{rx^r}\right)\left\{1 + \frac{1}{2!} \cdot \frac{3}{4} \cdot \frac{m^2}{x^r} + \cdots\right\}$$

$$\leqslant 9m^2/(8rx^r) \leqslant 9m^2/(40x^r). \tag{12}$$

From (6) and (11),

$$|\log z - (m-1) \log x| \leqslant 3m^2/(4rx^r). \tag{13}$$

From this and (12), we get that

$$z = x^{m-1}\left\{1 + \theta\left(\frac{9}{40} \cdot \frac{m^2}{x^r}\right)\right\}$$

$$= x^{m-1} + \theta\,\{9m^2/(40\,x^{r-m+1})\}$$

$$= x^{m-1} + \theta\,\{9m^2/(40x^2)\} = x^{m-1} + \theta\,(36/40)$$

$$= x^{m-1} + \theta\,(\cdot 9).$$

Therefore

$$x^{m-1} - \cdot 9 < z < x^{m-1} + \cdot 9. \tag{14}$$

But, from (5),

$$z \neq x^{m-1} \tag{15}$$

From (14), (15), it follows that z is not an integer, which is contrary to our assumption. Therefore

$$n(n+1)\cdots(n+m-1) \neq y^r.$$

THEOREM II: If Hypothesis A is true, then, when $m > 7$ and $m - 2 > r > (m+3)/2$,

$$n(n+1)\cdots(n+m-1) \neq y^r.$$

If possible, let

$$n(n+1)\cdots(n+m-1) = y^r.$$

Then arguing as in theorem I, we get that

$$\begin{aligned} &|r \log z - (m-1) r \log x - A_1/x^r| \\ &\leqslant \frac{1}{2}\cdot\frac{m^3}{3x^{2r}} + \frac{1}{3}\cdot\frac{m^4}{4x^{3r}} + \cdots \\ &= \frac{m^3}{x^{2r}}\left\{\frac{1}{6} + \frac{1}{12}\cdot\frac{m}{x^r} + \cdots\right\} \\ &\leqslant \frac{m^3}{x^{2r}}\left\{\frac{1}{6} + \frac{1}{48}\right\} = 3m^3/(16x^{2r}). \end{aligned} \tag{16}$$

Further

$$\left| e^{A_1/(rx^r)} - 1 - A_1/(rx^r) \right| \leqslant \frac{m^4}{r^2 x^{2r}}\left\{\frac{1}{2^2\cdot 2!} + \frac{1}{2^3\cdot 3!}\cdot\frac{m^2}{rx^r} + \cdots\right\}$$

$$\leqslant \frac{m^4}{r^2 x^{2r}}\left\{\frac{1}{8} + \frac{1}{240}\right\} = 31m^4/(240\, r^2 x^{2r}). \tag{17}$$

Again

$$\left| e^{3m^3/(16rx^{2r})} - 1 \right| \leqslant \frac{m^3}{rx^{2r}}\left\{\frac{3}{16} + \frac{1}{2!}\left(\frac{3}{16}\right)^2\cdot\frac{m^3}{rx^{2r}} + \cdots\right\}$$

$$\leqslant m^3/(4rx^{2r}) \tag{18}$$

From (16), (17), (18), we get that

$$z = x^{m-1}\left\{1 + A_1/(rx^r) + \theta\left(\frac{31}{240}\cdot\frac{m^4}{r^2x^{2r}}\right)\right\}\left\{1 + \theta\left(\frac{m^3}{4rx^{2r}}\right)\right\}$$

$$= x^{m-1} + A_1\cdot x^{m-1-r}/r + \theta\left(\frac{m^4 x^{m-1-2r}}{r}\right)\left\{\frac{31}{240r} + \frac{1}{4m} + \frac{m}{8rx^r} + \frac{m^3}{7\times 4r^2\cdot x^{2r}}\right\}$$

$$= x^{m-1} + A_1 x^{m-1-r}/r + \theta\,(m^4 x^{m-1-2r}/r)\left\{\frac{6\cdot 2}{240} + \frac{1}{28} + \frac{1}{600} + \frac{1}{11200}\right\}$$

$$= x^{m-1} + A_1 x^{m-1-r}/r + \theta\,(\cdot 062\, m^4 x^{m-1-2r}/r)$$

$$= x^{m-1} + A_1 x^{m-1-r}/r + \theta\,(\cdot 062 \times 16\cdot x^{m+3-2r}/r)$$

$$= x^{m-1} + A_1 x^{m-1-r}/r + \theta\,(\cdot 992/r).$$

Therefore

$$rx^{m-1} + A_1 x^{m-1-r} - \cdot 992 < rz < rx^{m-1} + A_1 x^{m-1-r} + \cdot 992 \quad (19)$$

Now A_1 is an integer and $m - 1 - r \geqslant 1$.

So rz is not an integer unless

$$rz = rx^{m-1} + A_1 x^{m-1-r}. \quad (20)$$

Now $r \leqslant m - 2$. So $m - 1 - r \geqslant 1$.

Further $(x, z) = 1$. So if (20) is true, we should have

$$r = Mx^{m-1-r}, \text{ where M is an integer.} \quad (21)$$

But $r \leqslant m - 2$ and by lemma (2), $x \geqslant m/2$.

So if (21) is true, we should have

$$M = 1 \text{ and } m - 1 - r = 1, \textit{ i.e.}, r = x. \quad (22)$$

But x is divisible by no prime $\leqslant m/2$.

Hence, since $r \leqslant m - 2$, if (22) is true, then

$$r = x = P, \text{ where P is a prime} > m/2. \quad (23)$$

But $(P^p \pm 1)$ $(P \pm 1)$ has got prime factors only of the form $2tP + 1$. (24)

From our assumption

$$z^r = (x^r - t) \cdots (x^r - 1)(x^r + 1) \cdots (x^r - t + m - 1).$$

Hence either $x^r - 1$ or $x^r + 1$ is a factor of z^r. But, if (20) is true, from (24), this number is a multiple of a prime of the form $2tP + 1$; and hence is a multiple of $(2tP + 1)^r$. So, if (20) is true, we get

$$x^r + 1 \geqslant (2P + 1)^r$$

i.e.,

$$x > 2P = 2x, \text{ from (23).}$$

But this is absurd. Hence (20) is not true. Therefore, from (19), we get that rz is not an integer. Consequently z is not an integer. So our assumption that

$$n(n + 1) \cdots (n + m - 1) = y^r$$

is wrong. Thus theorem II is completely proved.

THEOREM III: When $4 \leqslant m \leqslant 16$ and $r \geqslant m + 1$, $P(m) \neq y^r$.

In this case, every $P(m)$ satisfies hypothesis A. So Theorem I is applicable and hence we get this theorem.

THEOREM IV: When $7 \leqslant m \leqslant 16$ and $m - 2 \geqslant r \geqslant (m + 3)/2$,

$$P(m) \neq y^r.$$

This follows from lemma (1) and Theorem II.

THEOREM V: (Hayashi).

$$P(2) \neq y^r.$$

If $n(n+1) = y^r$, then $n = a^r$ and $n+1 = b^r$ and so $1 = b^r - a^r$, which has no solution except $b = 1$ and $a = 0$.

THEOREM VI: (Goldbach and Mille).

$$P(3) \neq y^r.$$

If possible, let

$$(n-1)\,n\,(n+1) = y^r.$$

Since n is prime to $(n-1)(n+1)$, we should have $n = a^r$ and $n^2 - 1 = b^r$. So $a^{2r} - b^r = 1$, which has no solution except $a = 1$ and $b = 0$.

THEOREM VII: (Andre)

$$P(m) \neq y^m.$$

If possible, let

$$n(n+1)\cdots(n+m-1) = y^m. \tag{25}$$

Since there are m increasing integers and their product is an mth power, we have

$$n < y < n+m-1. \tag{26}$$

From (25) and (26), it follows that

y^m is divisible by $y \pm 1$, which is absurd. So the theorem is proved.

THEOREM VIII: If hypothesis A is true,

$$n(n+1)\cdots(n+m-1) \neq y^{m-1}.$$

If possible, let

$$n(n+1)\cdots(n+m-1) = y^{m-1}.$$

Then, since Hypothesis A is true,

$$n+t = x^{m-1}$$

and $$n(n+1)\cdots(n+t-1)(n+t+1)\cdots(n+m-1) = z^{m-1}. \tag{27}$$

Obviously $(z, x) = 1$. So as in the previous theorem, we get that z^{m-1} is divisible by $z-1$ or $z+1$. Hence the theorem follows.

THEOREM IX: When $m \leqslant 16$,

$$P(m) \neq y^{m-1}.$$

This follows from lemma (1) and theorem VIII.

THEOREM A: (Stated in the Introduction). This is only a combination of Theorems III, IV, V, VI, VII and IX.

THEOREM X: If $f(x)$ is a polynomial with integral coefficients and having at least two different non-multiple integral roots, then the equation

$f(x) = ty^r$, where t and r are given positive integers and $r \geqslant 3$,

will have, if at all, only a finite number of solutions in integers.

Folllowing Polya, Landau and Oatrowosky this can be easily deduced from Thue-Siegel's theorem.

THEOREM B: (Stated before)

This is only a particular case of Theorem X.

THEOREM C: (Stated before)

If possible, let

$$n(n+1)\cdots(n+m-1) = y \tag{28}$$

Let $p_1, p_2, \cdots, p_t$ be the different primes not exceeding m. Then from (28)

$$n = p_1^{a_1}\cdots p_t^{a_t} x^r, \text{ where } 0 \leqslant a_s \leqslant r-1,\ s = 1, \cdots, t$$

and

$$n+1 = p_1^{b_1}\cdots p_t^{b_t} z^r, \text{ where } 0 \leqslant b_s \leqslant r-1,\ s = 1, \cdots, t.$$

Therefore

$$1 = p_1^{b_1}\cdots p_t^{b_t} z^r - p_1^{a_1}\cdots p_t^{a_t} x^r \tag{29}$$

If $b_s \geqslant 1$, then $a_s = 0$ and conversely. (30)

From lemma (4), if $b_s \geqslant m$, then $b_s \geqslant r-m$. (31)

Similarly, if $a_s \geqslant m$, then $a_s \geqslant r - \mathrm{m}$. (32)

If $b_s \geqslant m$, multiply (29) by p^{r-b_s}

and if $a_s \geqslant m$, multiply (29) by p^{r-a_s}.

Now from (31), $r - b_s \leqslant m$ when $b_s \geqslant m$ and from (32), $r - a_s \leqslant m$ when $a_s \geqslant m$ (See lemmas (5) and (6)).

By performing this multiplication for every a and b greater than m, from (30), (29) is transformed to

$$p_1^{a_1}\cdots p_t^{a_t}\ \mathrm{X}^r - p_1^{\beta_1}\cdots p_t^{\beta_t}\cdots \mathrm{Y}^r = p_1^{\gamma_1}\cdots p_t^{\gamma_t},$$

where $0 \leqslant \alpha_s, \beta_s, \gamma_s \leqslant m$.

This means that

$$\mathrm{AX}^r - \mathrm{BY}^r = \mathrm{C}, \tag{33}$$

where A, B, C are each less than

$$(p_1 p_2 \cdots p_t)^m. \tag{34}$$

But Siegel has proved that (33) has no solution when $r >$ F (ABC) (35)

Further from (34),

$$\mathrm{ABC} \leqslant (p_1\cdots p_t)^{3m} = \chi(m). \tag{36}$$

From (36), (33) and (35), the theorem follows.

METHODS OF GENERATING DIFFERENTIAL INVARIANTS WITH SPECIAL REFERENCE TO PATH-SPACES OF ORDER 2*

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(Communicated by Prof. A. Narasinga Rao)

We briefly sketch below, two methods of generating differential invariants, the one due to Prof. D. D. Kosambi,[1] and the other to Prof. Elie Cartan[2] of Paris. We are mainly concerned with the fact that these apparently different methods lead us to the same results and are not at variance as was believed by Prof. Cartan.[3]

For illustration, let us consider path-spaces of order 2, *i.e.*, A space wherein the system of paths is defined by differential equations of order 3, *viz.*,

$$x^{(3)i} + a^i(x, x^{(1)}, x^{(2)}, t) = 0 \qquad \text{I}$$

We assume that I and their equations of variation, *viz.*,

$$u^{(3)\,i} + a^i_{(2)\,k}\, u^{(2)\,k} + a_{(1)\,k}^{\;i}\, u^{(1)\,k} + a^i_{(0)\,k}\, u^k = 0 \qquad \text{II}$$

are tensor invariant under the transformation group

$$(\text{T}) \qquad x^i = \phi^i(x^1\, x^2 \cdots x^n),\ \bar{t} = t$$

$$\left|\frac{\partial \bar{x}^i}{\partial x^j}\right| \neq \text{zero}.$$

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* Read at the Symposium on "Generalised Geometry" during the Eleventh Indian Mathematical Society's Conference held at Hyderabad (Deccan)(December 1939).

For notation please refer to D. D. Kosambi, "Path-Spaces of Higher Order," *Quart. Jour. of Maths.*, 1936, **7**, 97–104.

[1] D. D. Kosambi, "Problem of Differential Invariants," *Jour. I. M. Soc.*, 1934, **20**, 185–88.

[2] E. Cartan, *Math. Zeit.*, 1933, **37**, 619.

[3] In a letter to Prof. D. D. Kosambi received Feb. 25, 1938.

Equations II can be expressed in the tensorial form

$$D^3 u^i + \underset{2}{P}{}^i_r \ (D^2 u^r) + \underset{1}{P}{}^i_r \ (D\, u^r) + \underset{0}{P}{}^i_r \ u^r = 0$$

where

$$D\, u^i \equiv u^{(1)\, i} + \gamma^i_k \, u^k$$

$$\underset{2}{P}{}^i_r = \alpha^i_{(2)\, r} - 3\gamma^i_r$$

$$\underset{1}{P}{}^i_r = \alpha^i_{(1)\, r} - 3\,(\gamma^{(1)\, i}_{\ \ r} + \gamma^i_k \, \gamma^k_r)$$

$$\underset{1}{P}{}^i_r = \alpha^i_{(0)\, r} - \alpha^i_{(1)\, k} \, \gamma^k_r - \gamma^{(2)\, i}_{\ \ r} + 2\gamma^{(1)\, i}_{\ \ k} \, \gamma^k_r - 2\gamma^i_k \, \gamma^{(1)\, k}_{\ \ r} + 2\gamma^i_k \, \gamma^k_l \, \gamma^l_r.$$

These give us the primary tensors $\underset{0}{P}{}^i_r$ and $\underset{1}{P}{}^i_r$ the third being equated to zero to give us an intrinsic connection $\gamma^i_r = \frac{1}{3} \, \alpha^i_{(2)\, r}$. Alternating the two differential operators D and $\underset{2}{\nabla}_i \equiv \dfrac{\partial}{\partial \dot{x}^i}$ successively we get two more differential operators $\underset{1}{\nabla}_i$ and $\underset{0}{\nabla}_i$ defined by

$$\underset{1}{\nabla}_i = \frac{\partial}{\partial x^{(1)\, i}} - 2\gamma^k_i \, \frac{\partial}{\partial x^{(2)\, k}}.$$

$$\underset{0}{\nabla}_i \, u^k = u^k_{(0)\, i} - \gamma^l_i \, \underset{1}{\nabla}_l \, u^k + \underset{0}{\overset{2}{Q}}{}^l_i \, \underset{2}{\nabla}_l \, u^k + (\underset{1}{\nabla}_i \, \gamma^k_l) \, u^l.$$

All the differential invariants of the space under consideration should be derivatives of α^i of various orders. The first derivatives $\alpha^i_{(0)\, j}$, $\alpha^i_{(1)\, j}$ give us essentially $\underset{0}{P}{}^i_j$ and $\underset{1}{P}{}^i_j$. But $\alpha^i_{(2)\, j}$ is not a tensor and gives us the intrinsic connection of the space. Derivatives of $\alpha^i_{(2)\, j}$ and hence of γ^i_j should give us invariants of rank 2. $\gamma^i_{j\,(2)\, k}$ is the only tensor that is got this way. $\underset{1}{\nabla}_k \, \gamma^r_i$ is not a tensor. It is of the nature of the christoffel symbols of the Riemannian Space and has the transformation law,

$$(\underset{1}{\overline{\nabla}}_r \, \overline{\gamma}^m_l) = (\underset{1}{\nabla}_k \, \gamma^i_j) \, \frac{\partial x^k}{\partial \overline{x}^r} \, \frac{\partial \overline{x}^m}{\partial x^i} \, \frac{\partial x^j}{\partial \overline{x}^l} + \frac{\partial^2 x^m}{\partial x^j \partial x^i} \, \frac{\partial x^i}{\partial \overline{x}^r} \, \frac{\partial x^j}{\partial \overline{x}^l}.$$

Here, the second term on the right is purely a point function and hence vanishes when differentiated with respect to $\ddot{x}$ and $\dot{x}$. So we get $\underset{2}{\nabla}_l \, \underset{1}{\nabla}_k \, \gamma^i_j$ and $\underset{1}{\nabla}_l \, \underset{1}{\nabla}_k \, \gamma^i_j$ are tensors. We are able to express the former in terms of the I^i_j's and $\gamma^i_{j\,(2)\, k}$, and the latter is an independent tensor. Hence

$\underset{0}{P}{}^i_j$, $\underset{1}{P}{}^i_j$, $\gamma^i_{j(2)k}$, $\underset{1}{\nabla}_k \, \underset{1}{\nabla}_j \, \gamma^i_r$ along with $\dot{x}^i$, appear to be the basic set of differential invariants.

This has been supported[4] by the usual process of alternating all the differential operations, taken two at a time. All the invariants occur as coefficients on the right hand side and all these coefficients are expressible in terms of the basic set of invariants.

All these observations have been worked out also for differential equations of order $(\sigma + 1)$[5] and lead us to the result that

$$x^{(1)\,i},\ \underset{\gamma}{\mathrm{P}}{}^{i}_{j}\ (\gamma = 0,\ 1,\ \cdots \sigma - 1),\ \gamma^{i}_{j\,(\sigma)\,k},\ \text{and}\ \underset{1}{\nabla}_{k}\ \underset{1}{\nabla}_{j}\ \gamma^{i}_{r}$$

form the basic set of tensors for path-spaces of orders σ.

Let us now consider *Cartan's method*[6] of generating invariants for $\sigma = 2$, which is an immediate consequence of his own researches in the theory of continuous groups. He considers the Pfaffians.

$$(1)\qquad \begin{cases} \omega^i = dx^i - \dot{x}^i\, dt \\ w^i = d\dot{x}^i - \ddot{x}^i\, dt + \delta^i_k\, \omega^k \\ \theta^i = d\ddot{x}^i + a^i\, dt + \lambda^i_k\, w^k + \mu^i_k\, \omega^k \end{cases}$$

and $\omega^j_i = \gamma^j_i\, dt + \gamma^j_{ik}\, \omega^k$ defines the connection.

Then if we calculate

$$(2)\qquad \begin{cases} \Omega^i = -[\omega^i]' + [\omega^k\, \omega^i_k] + [w^i\, dt] \\ \Pi^i = -[w^i]' + [w^k\, \omega^i_k] + [\theta^i\, dt] \\ \ominus^i = -[\theta^i]' + (\theta^k\, \omega^i_k] \\ \Omega^j_i = -[\omega^j_i]' + [\omega^k_i\, \omega^j_k] \end{cases}$$

the square brackets having the significance

$$[\omega^k\, \omega^i_k] \equiv (\omega^k_\delta\, \omega^i_{dk} - \omega^k_d\, \omega^i_{\delta k})$$

where d and δ are distinct but interchangeable displacements, the invariants should appear in the right hand side.

We find that

$$(3)\qquad \Omega^i = (\gamma^i_{jk} - \gamma^i_{jk})\, \omega^k_\delta\, \omega^j_d + (\delta^i_k - \gamma^i_k)\, (\omega^k_d\, \delta_t - \omega^k_\delta\, dt)$$

$(\delta^i_k - \gamma^i_k)$ is one invariant of the connection and $(\gamma^i_{jk} - \gamma^i_{kj})$ is another. Cartan makes both of them vanish in the one case to reduce the number of invariants of the connection and in the other to get symmetric christoffel symbols.

---

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[5] ———— *Proc. Lond. Math. Soc.*, 1939, **45**, Series 2.

[6] Elie Cartan—in the letter to Prof. Kosambi cited before.

Then

$$
\begin{aligned}
(4)\quad \Pi^i = {} & (w_d^k\,\delta t - w_\delta^k\,dt)\,(\lambda_k^i - 2\gamma_k^i) \\
& + (\omega_d^k\,\delta t - \omega_\delta^k\,dt)\,(\mu_k^i - \gamma^{(1)}{}_k^i + \gamma_h^i\,\gamma_k^h) \\
& + (w_d^h\,\omega_d^k - w_\delta^h\,\omega_d^k)\,(\gamma_{k\,(1)\,h}^i - \lambda_h^l\,\gamma_{k\,(2)\,l}^i - \gamma_{hk}^i) \\
& + (\omega_\delta^k\,\omega_d^h)\,\{(\gamma_{k\,(0)\,h}^i - \gamma_h^l\,\gamma_{k\,(1)\,l}^i - \mu_h^l\,\gamma_{k\,(2)\,l}^i) - (\gamma_{h\,(0)\,k}^i - \gamma_k^l\,\gamma_{h\,(1)\,l}^i - \mu_k^l\,\gamma_{k\,(2)l}^i)\} \\
& + (\omega_\delta^k\,\theta_d^h - \omega_d^k\,\theta_\delta^h)\,\gamma_{k\,(2)\,h}^i.
\end{aligned}
$$

This gives $\lambda_k^i = 2\gamma_k^i$ and $\mu_k^i = \gamma^{(1)}{}_k^i - \gamma_h^i\,\gamma_k^h$. We observed that Cartan keeps γ_{hk}^i symmetric so that he gets $\gamma_{hk}^i = \frac{1}{2}\,(\underset{1}{\nabla}_h\,\gamma_k^i + \underset{1}{\nabla}_k\,\gamma_h^i)$. But we keep $\gamma_{hk}^i = \underset{1}{\nabla}_k\,\gamma_h^i$ and we get $\gamma_{hk}^i - \gamma_{kh}^i$ to be the torsion tensor $(\underset{1}{\nabla}_k\,\gamma_h^i - \underset{1}{\nabla}_h\,\gamma_k^i)$. We make this slight relaxation in his conditions as it makes further calculations much simpler. Besides this has the added advantage of making one of the basic invariants, *viz.*, $\underset{1}{\nabla}_k\,\underset{1}{\nabla}_j\,\gamma_r^i$ occur explicitly as one of the coefficients (*vide* formula 6).

So we get once again,

$$
\begin{aligned}
(4\,a)\quad \Pi^i = {} & (w_d^h\,\omega_\delta^k - w_\delta^h\,\omega_d^k)\,(\underset{1}{\nabla}_h\,\gamma_k^i - \underset{1}{\nabla}_k\,\gamma_h^i) \\
& + (\omega_\delta^k\,\theta_d^h - \omega_d^k\,\theta_\delta^h)\,\gamma_{k\,(2)\,h}^i \\
& + (\omega_\delta^k\,\omega_d^h\,[\tfrac{1}{3}\,(\underset{1}{\nabla}_k\,\underset{1}{P}{}_h^i - \underset{1}{\nabla}_h\,\underset{1}{P}{}_k^i) + D\,(\underset{1}{\nabla}_k\,\gamma_h^i - \underset{1}{\nabla}_h\,\gamma_k^i) \\
& \qquad + \gamma_{k\,(2)\,m}^i\,\underset{1}{P}{}_h^m - \gamma_{h\,(2)\,m}^i\,\underset{1}{P}{}_k^m].
\end{aligned}
$$

$$
\begin{aligned}
(5)\quad \ominus^i = {} & (\theta_d^h\,\delta t - \theta_\delta^h\,dt)\,(\alpha_{(2)\,h}^i - 3\gamma_h^i) \\
& + (\theta_d^h\,w_\delta^k - \theta_\delta^h\,w_d^k)\,2\gamma_{k\,(2)\,h}^i \\
& + (\theta_d^h\,\omega_\delta^k - \theta_\delta^h\,\omega_d^k)\,(D\gamma_{k\,(2)\,h}^i + \underset{1}{\nabla}_h\,\gamma_k^i - \underset{1}{\nabla}_k\,\gamma_h^i) \\
& + w_d^h\,w_\delta^k\,[2\,(\underset{1}{\nabla}_h\,\gamma_k^i - \underset{1}{\nabla}_k\,\gamma_h^i)] \\
& + (w_d^k\,\delta t - w_\delta^k\,dt)\,\underset{1}{\Gamma}{}_k^i + (\omega_\delta^k\,\delta t - \omega_\delta^k\,dt)\,\underset{0}{P}{}_k^i \\
& + (\omega_\delta^h\,w_d^k - \omega_d^h\,w_\delta^k)\,[\tfrac{5}{6}\,(\underset{1}{\nabla}_h\,\underset{1}{P}{}_k^i - \underset{1}{\nabla}_k\,\underset{1}{P}{}_h^{c_i}) + \tfrac{3}{2}\,D\,(\underset{1}{\nabla}_h\,\gamma_k^i - \underset{1}{\nabla}_k\,\gamma_h^c) \\
& \qquad - \tfrac{1}{2}\,\underset{2}{\nabla}_h\,\underset{0}{P}{}_k^i - \tfrac{1}{2}\,D^2\gamma_{k\,(2)\,h}^i - \tfrac{1}{2}\,\underset{1}{P}{}_r^i\,\gamma_{k\,(2)\,h}^r \\
& \qquad + \tfrac{3}{2}\,\gamma_{h\,(2)\,r}^i\,\underset{1}{P}{}_k^r - 2\gamma_{k\,(2)\,r}^i\,\underset{1}{P}{}_h^r] \\
& + \omega_d^h\,\omega_\delta^k\,[\tfrac{1}{3}\,(\underset{1}{\nabla}_k\,\underset{1}{P}{}_h^i - \underset{1}{\nabla}_h\,\underset{1}{P}{}_k^i) + D\,(\underset{1}{\nabla}_k\,\gamma_h^i - \underset{1}{\nabla}_h\,\gamma_k^i) \\
& \qquad - \gamma_{k\,(2)\,r}^i\,(D\underset{1}{P}{}_h^r - \underset{0}{P}{}_h^r) + \gamma_{h\,(2)\,r}^i\,(D\underset{1}{P}{}_k^r - \underset{0}{P}{}_k^r) \\
& \qquad + \underset{1}{P}{}_h^r\,D\gamma_{k\,(2)\,r}^i - \underset{1}{P}{}_k^r\,D\gamma_{h\,(2)\,r}^i].
\end{aligned}
$$

This gives $\gamma^i_h = \frac{1}{3}\, a^i_{(2)\,h}$ to be an intrinsic connection. We have made use of this value in expressing the other coefficients in terms of known invariants.

$$
\begin{aligned}
(6)\qquad \Omega^j_i = {} & (\theta^k_d\, \delta t - \theta^k_\delta\, dt)\, \gamma^j_{i\,(2)\,k} \\
& + (w^k_d\, \omega^h_\delta - w^k_\delta\, \omega^h_d)\, (\underset{1}{\nabla}_k\, \underset{1}{\nabla}_h\, \gamma^j_i) \\
& + (\theta^k_d\, \omega^h_\delta - \theta^k_\delta\, \omega^h_d)\, (\underset{2}{\nabla}_k\, \underset{1}{\nabla}_h\, \gamma^j_i) \\
& + (\omega^k_d\, \delta t - \omega^k_\delta\, dt)\, [\tfrac{1}{2}\, \underset{2}{\nabla}_h\, \underset{0}{P^i_k} + \tfrac{1}{2}\, D^2\, \gamma^i_{k\,(2)\,h} + \tfrac{1}{2}\, \underset{1}{P^i_r}\, \gamma^r_{k\,(2)\,h} \\
& \qquad - \tfrac{3}{2}\, \gamma^i_{r\,(2)\,h}\, \underset{1}{P^r_k} + \gamma^i_{k\,(2)\,r}\, \underset{1}{P^r_h} \\
& \qquad + \tfrac{1}{2}\, (\underset{1}{\nabla}_k\, \underset{1}{P^i_h} - \underset{1}{\nabla}_h\, \underset{1}{P^i_k}) \\
& \qquad + \tfrac{3}{2}\, D\, (\underset{1}{\nabla}_k\, \gamma^i_h - \underset{1}{\nabla}_h\, a^i_k)] \\
& + \omega^k_d\, \omega^h_\delta\, [K^j_{ihk} + \underset{1}{P^l_k}\, (\underset{2}{\nabla}_l\, \underset{1}{\nabla}_h\, \gamma^j_i) - \underset{1}{P^l_h}\, (\underset{2}{\nabla}_l\, \underset{1}{\nabla}_r\, \gamma^j_i)]
\end{aligned}
$$

where K^j_{ihk} is the coefficient of u^r in $[\underset{0}{\nabla}_k\, \underset{0}{\nabla}_j - \underset{0}{\nabla}_j\, \underset{0}{\nabla}_k]\, u^i$.

From formulæ (3–6) it can be seen that even by the methods of Cartan we are led to the same basic set of tensors. This should give us no surprise inasmuch as the foundation of both the methods is the same, *viz.*, alternation of fundamental operations. But Cartan displays the rôle of the differential invariant without showing their independence or inter-dependence. The method of Kosambi goes directly to the question of setting up a basis for the tensorial operators and by alternating these deduces the fundamental set of independent differential invariants, from which all the others can be generated. Here the question of interpretation is of minor import.

EFFECT OF TEMPERATURE ON THE RAMAN SPECTRUM OF QUARTZ

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1. *Introduction*

The importance of quartz in the mineral world, its many useful properties and practical applications have naturally made the crystal the subject of intensive scientific research in many directions.[32] In particular, the fact that clear pieces of crystalline quartz are generally to be found in laboratories has encouraged numerous investigations on the scattering of light and the Raman effect in the substance. Nevertheless, the topic is far from being exhausted. A study of the relevant literature (a complete bibliography of which is appended to this paper) shows that much experimental and theoretical research is necessary before we can claim to have fully understood the significance of the data. In particular, a correct and complete classification of the numerous lines observed in the spectrum and their assignment to definite modes of vibration within the crystal have yet to be accomplished. Further, in view of the fact that quartz undergoes a sudden polymorphic transition at 575° C. at which its symmetry and properties change reversibly, the thorough study of the Raman spectra at high temperatures is of special importance. The information so far available on this point is rather meagre and incomplete. In these circumstances, a careful and detailed investigation of the spectrum with particular reference to the influence of temperature was undertaken by the present author.

2. *Experimental*

The investigation was carried out with clear cylindrical pieces of quartz crystal (2″ long and 1″ diameter) supplied by a firm at Tanjore. For studying the thermal effect on the spectrum, a special furnace capable of withstanding a temperature of about 800° C. and with suitable holes for the incident and scattered light to pass through, was made use of. The temperatures were measured by an iron-constantan thermo-couple with the hot junction kept touching the crystal. Temperature measurements were correct to ± 5° C. The scattered light was observed against a distant dark background.

To obtain the spectrum at liquid-air temperature the crystal was held in a vertical position inside an unsilvered Dewar's flask and the scattered

light was reflected on the slit of the spectrograph by means of a right-angled prism. The spectrum was obtained in an exposure time of 15 hours.

A sphere of quartz which could be easily oriented along definite directions in the crystal was used for longitudinal observation of the scattered light. The experimental arrangement was the same as the one described by the author elsewhere.

The present study was carried out with a Hilger two-prism spectrograph of high light-gathering power. The plates were measured on a Hilger cross-slide micrometer with an iron arc comparison. The frequency measurements in the case of sharp lines were correct to $\pm$ 1 wave-number.

3. *Fundamental Frequencies*

The enlargement of an intense spectrum of quartz with the minimum of background is reproduced in Fig. 1 of the Plate. The frequencies of the Raman shifts (in wave-numbers per centimeter) observed by the author are listed in Col. 3 of Table I. The numbers in brackets by their side give the intensities of the lines recorded by visual estimate. Fifteen definite fundamental frequencies have been observed in the spectrum. They generally agree well with those reported by Rasetti.[14] It has been possible to separate the line 397 excited by the λ 4358 radiation from the strong line 465 excited by λ 4347 of mercury with which it is liable to be confused if a spectrograph of smaller dispersion is used for recording the spectrum. A weak line at 404 recorded by Rasetti using λ 2537 excitation could not, however, be observed in the present case with the λ 4358 excitation as it is superposed on the line 465 excited by λ 4347. The same line excited by λ 4046 could not also be observed because of its coincidence with the diffuse line 207 excited by λ 4078. In the present investigation an extra weak line 453 which has not been observed by Rasetti could be just separated from the strong line 465. The existence of this line in the spectrum has already been indicated by the polarisation studies of Cabannes and Bouhet.[30] The line which is generally referred to as the 800 line is very well seen to be a doublet with frequency shifts 794 and 805. Fig. 1 shows clearly the two lines 1064 and 1082 reported by some authors as a single line at 1074. Some of the above features can be better seen in the spectrogram at 25° C. included in Fig. 3. It has been further observed that in the spectrum of light scattered along the optic axis with transverse illumination, the line 1082 of the doublet disappears and 1064 persists.

Longitudinal Scattering of Light.—Figs. 2 *a* and 2 *b* are the spectra of the light scattered backwards with the illumination respectively along and perpendicular to the optic axis, the incident light being unpolarised. It will

be observed that in the light scattered along the optic axis the line 263 and the doublet at 800 disappear whereas for the perpendicular direction they appear clearly. It must be remarked that similar observations have been made by Cabannes and Bouhet[30] when the incident light is circularly polarised. This special behaviour of these lines have enabled these authors to identify them as degenerate oscillations of a type different from the rest.

The author has made a special search for the doubtful and zero-intensity lines reported by Gross and Romanova[11] and others by taking very intense and over-exposed spectrograms, but has failed so far to observe any of these. If the lines are really genuine they are probably the combination frequencies of the more intense lines in the spectrum as is seen below :—

$207 + 127 \approx 320$ $\quad$ $397 + 354 \approx 746$
$397 + 127 \approx 526$ $\quad$ $805 + 127 \approx 944$
$465 + 127 \approx 585$ $\quad$ $805 + 207 \approx 1021$
$354 + 263 \approx 633$

4. Influence of Temperature

Intense spectrograms taken at a series of temperatures,—192, 25, 100, 200, 300, 410 and 530° C. are reproduced in Fig. 3 of the Plate. In Figs. 4 and 5 are given the microphotometer records for the spectra at 25 and 410° C. respectively. The curve at 530° C. could not be obtained due to the background in the negative. The frequencies of the Raman lines at the temperature of the liquid air, at room temperature and at 530°C. are listed in Table I. Tables II, III and IV give the variations in the frequencies as well as the

TABLE I

Raman Shift in Quartz $\quad$ *Excitation* λ — 4358

No.	Temperature			No.	Temperature		
	−192° C.	25° C.	530° C.		−192°C.	25°C.	530° C.
1	132	127 (20)	98	9	..	691 (3)	682
2	220	207 (15 *d*)	130–212	10	802	794 (3)	784–805
3	266	263 (4)	252	11		805 (3)	
4	355	354 (6)	350	12	..	1064 (2)	1052–1070
5	397	397 (4)	393	13		1082 (2)	
6	..	453	..	14	1160	1158 (5)	1154
7	468	465 (30)	455	15	..	1228 (2)	1223
8	..	501 (1)					

TABLE II

$\nu = 127$ cm.$^{-1}$

1 Temperature in °C.	2 Maximum of the line	3 Shift $\Delta\nu$	4 Lower limit of the line	5 Upper limit of the line	6 Breadth in cm.$^{-1}$ 4 ~ 5
− 192	132	0	..	..	..
25	127	5	122	130	8
100	125	7	120	128	8
200	121	11	115	128	13
300	115	17	110	126	16
410	108	24	98	117	19
530	98	34	88	112	24

TABLE III

$\nu = 207$ cm.$^{-1}$

1 Temperature in °C.	2 Centre of the line	3 Shift $\Delta\nu$	4 Lower limit of the line	5 Upper limit of the line	6 Breadth in cm.$^{-1}$ 4 ~ 5
− 192	220	0	..	..	..
25	207	13	196	216	20
100	205	15	194	216	22
200	197	23	181	214	33
300	187	33	165	210	45
410	177	43	146	208	62
530	171	49	130	212	82

TABLE IV

$\nu = 465$ cm.$^{-1}$

1 Temperature in °C.	2 Maximum of the line	3 Shift $\Delta\nu$	4 Lower limit of the line	5 Upper limit of the line	6 Breadth in cm.$^{-1}$ 4 ~ 5
−192	468	0	..	..	..
25	465	3	458	470	12
100	464	4	458	469	11
200	462	6	455	470	15
300	460	8	448	468	20
410	458	10	444	470	26
530	455	13	440	471	31

breadths of the three most intense lines 127, 207 and 465. The lines constituting the doublets at 800 and 1,070 merge out into one another at high temperatures and hence the breadths and frequency shifts of the individual lines have not been tabulated. For the rest of the lines the magnitudes of the changes were not marked so as to necessitate their detailed recording.

The increase of Rayleigh scattering at higher temperatures is easily observable in the spectrograms. Further, the general observations of the earlier authors that the anti-stokes lines increase in intensity as the temperature of the crystal is raised, is beautifully confirmed by the present work. As can be seen from Fig. 3, the anti-stokes of the line 465 is not recorded at all at − 192° C. At room temperature it is much weaker than the stokes line. As the temperature is raised still further, the anti-stokes line becomes gradually brighter and tends, as might be expected from Placzek's[33] theory, to equal the intensity of the stokes line. Yet it must be remarked that even at 530° C. it is not as intense as the stokes line. Nothing definite can be said, however, about the variation in the intensity of the stokes line with rise of temperature, as the detection of the small changes, if any, requires quantitative estimation.

An interesting observation made in the present investigation is the difference between the changes with temperature in the character of the three intense lines in the spectrum. It can be seen from Fig. 3 that at liquid air temperature all the three lines 127, 207 and 465 are almost equally sharp. However, at room temperature the line 207 is diffuse while the other two remain sharp. As the temperature is increased all these lines broaden ; but

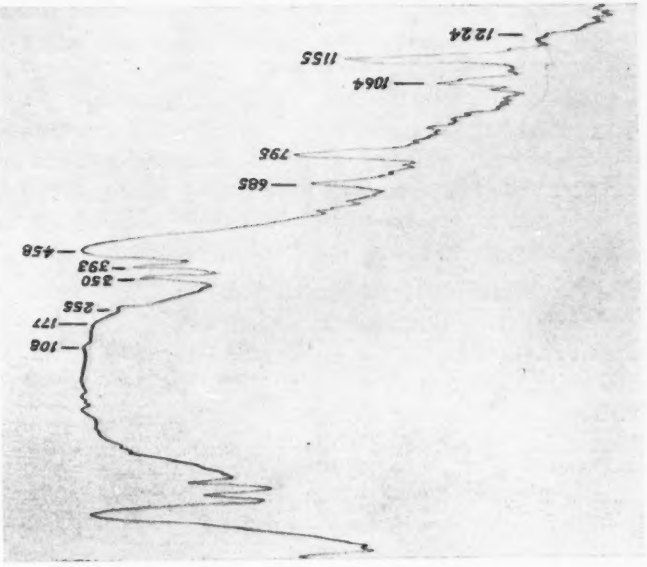

FIG. 5

Microphotometer Curve : Crystal at 410° C.

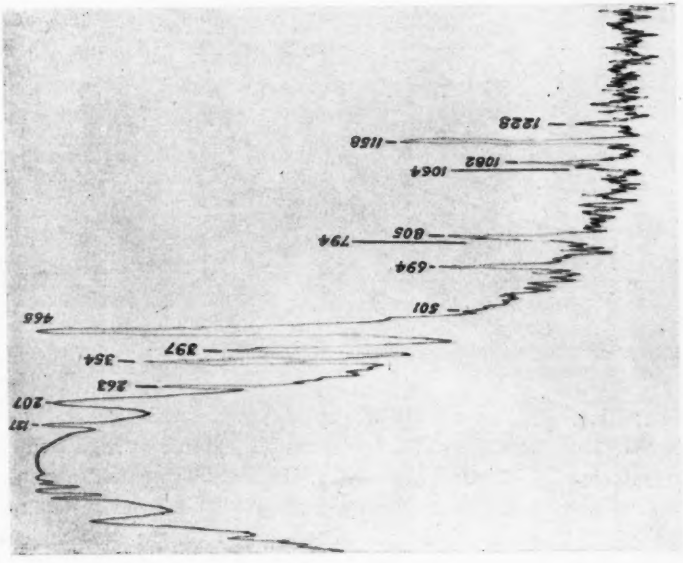

FIG. 4

Microphotometer Curve : Crystal at 25° C.

the rate at which the 207 line broadens is much more than that of the other two. At 530° C. this line is so broad and simultaneously weakened in intensity that it is practically washed out of the spectrum. In contrast with this, the other two lines, though broader, are nevertheless, very prominent in the spectrogram at 530° C. Further, it is noteworthy that this broadening of the 207 line is unsymmetrical inasmuch as the outer edge of the band is always approximately limited by the original position of the line. The shift of the line 127 is much more pronounced than the broadening; it shifts bodily to lower frequency as the temperature is increased. The broadening of the 465 line also appears to be unsymmetrical.

The curves showing the breadths of the lines as a function of temperature are given in Fig. 6. Fig. 7 shows the relation between the frequency shifts and temperature. The curve for the line 207 is not included in the latter as the exact frequency of the line at high temperatures is quite indefinite due to its large breadth.

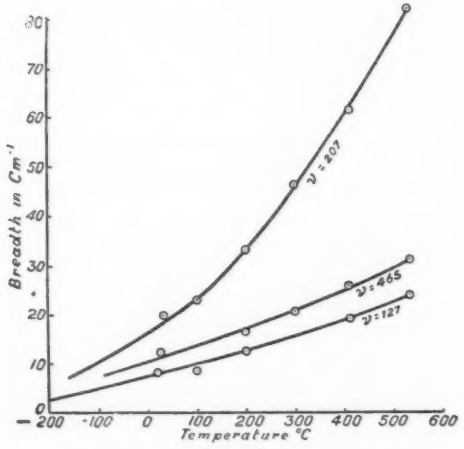

FIG. 6

Variation in the breadths of lines with temperature

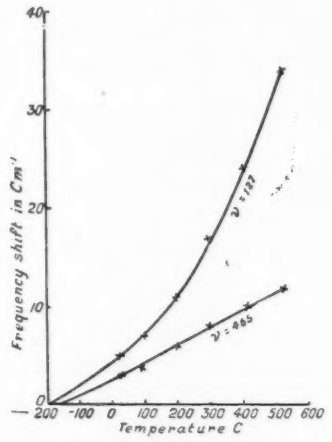

FIG. 7

Change of frequency of Raman lines with temperature

As regards the other lines in the spectrum it can be generally said that all of them broaden out and shift to observable extents at high temperatures. The three lines 263, 354 and 397 are sufficiently sharp and strong at high temperatures as to make them conspicuously visible even in the spectrum taken at 530° C. The line 263 is shifted to a larger extent than the other two. The line 694 is also shifted considerably at high temperatures. The doublet at 800 appears at 530° C. as a band extending over 20 cm.$^{-1}$ and the one at

1070 becomes a band with a sharp maximum at 1061. It appears further that the line 1158 grows much weaker as the temperature is increased.

5. *Significance of the Results*

The extraordinary behaviour of the 207 line at high temperatures appears to be of special significance. It is well known that many of the physical properties of quartz undergo remarkable changes at and preceding the transition temperature, 575° C. The coefficient of thermal expansion as measured by Jay[34] both parallel and perpendicular to the optic axis, increases anomalously above 200° C. and becomes infinite at the transition temperature. The measurements of the Young's modulus at various temperatures carried out by Perrier and Mandrot[35] show the rapid fall at and preceding the transition. Further, the curve showing the variation of piezo-electric activity with temperature obtained by Pitt and Mckinley[36] indicates that this begins to fall at about 200° C. and reaches a zero value near the transition point. It is interesting to note that the rapid rate at which the 207 line, in particular, broadens is quite analogous to the variations in the physical properties cited above. It appears, therefore, that the particular oscillation represented by this line and the deformation of the atomic grouping resulting from its excitation is specially responsible for these changes in physical properties and ultimately also for the α-β transformation of quartz. In fact, the behaviour of the line clearly indicates that the forces controlling this oscillation weaken with rising temperature and ultimately vanish at the transition temperature. The identification of the particular mode of oscillation which gives rise to the 207 line is therefore of importance for the theory of the α–β trnasformation.

The record of a complete spectrum of β quartz is of special interest as its increased symmetry should manifest itself by notable absence of certain frequencies. Hence, attempts were made to obtain the same by keeping the crystal heated at a temperature above the transiton point. But in all trials, the crystal broke into fragments when it was heated through the transition temperature in spite of very gradual increase of temperature and uniformity of the temperature field inside the furnace. However, the author hopes to record the same by the use of a small crystal under better experimental conditions.

In conclusion, the author wishes to record his grateful thanks to Prof. Sir C. V. Raman for his great interest in the present work.

6. *Summary*

Fifteen fundamental frequencies of internal vibrations are established for quartz from a careful study of its Raman spectrum, their values at room

temperature being 127, 207, 263, 354, 397, 453, 465, 501, 694, 794, 805, 1064, 1082, 1158 and 1228. Three of these lines 263, 794 and 805, are found to vanish in the spectrum of the light scattered longitudinally along the optic axis when the incident light is unpolarised. The thermal behaviour of the Raman lines over a wide range of temperature starting from that of liquid air to 530° C. has also been studied. All the lines are observed to broaden and shift to lower frequencies as the temperature of the crystal is raised. The line 207, however, behaves in an exceptional manner, broadening enormously at higher temperatures and in an unsymmetrical manner with respect to its original position, ultimately disappearing into a continuum as the transition temperature of 575° C. is approached. The behaviour of the 207 line with rise of temperature runs parallel to the changes in the physical properties of quartz such as thermal expansion, elastic moduli and piezo-electric activity which precede the transition from the α to the β form. From this fact it would appear that the particular mode of oscillation giving rise to the line 207 is responsible in special measure for these changes and ultimately for the transition itself.

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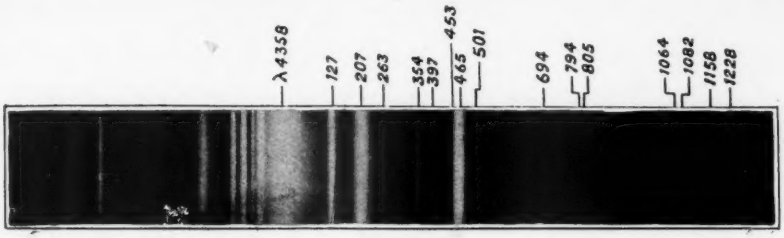

Fig.1

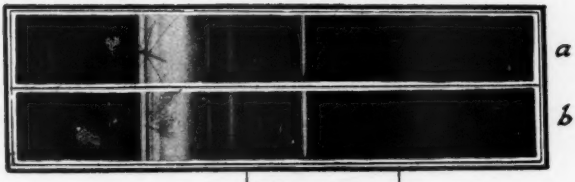

Fig. 2

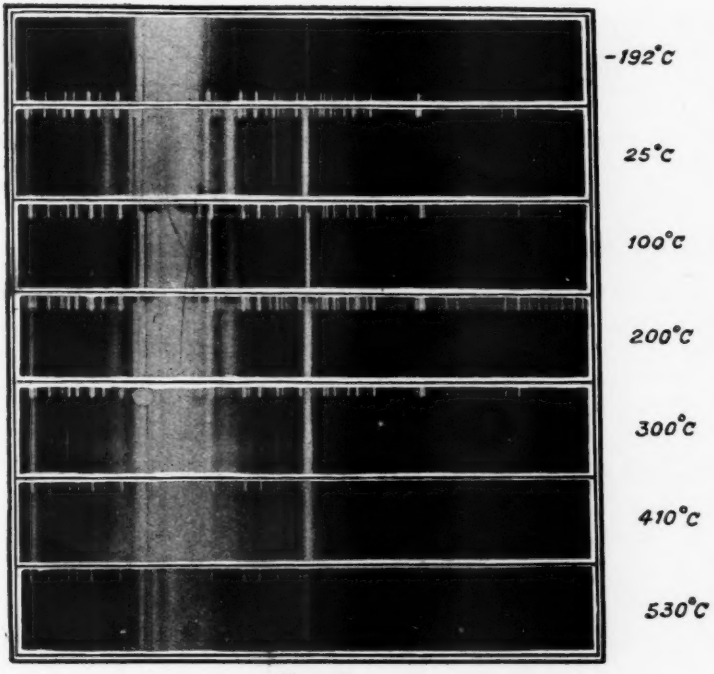

Fig.3

Raman Spectrum of Quartz

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COLOUR IN RELATION TO CHEMICAL CONSTITUTION OF THE ORGANIC SALTS AND METALLIC DERIVATIVES OF ISONITROSO-DIPHENYL-THIOHYDANTOIN

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Received November 11, 1939

In accordance with the " Theory of colour on the basis of molecular strain" advanced by Dutt,[1] the nitroso group is the most fruitful cause of intense colour amongst organic compounds on account of the high degree of molecular strain contained therein, as calculated from theoretical considerations. This is the reason why most of the well-known true nitroso compounds have very high absorption as can be seen from Table I.

Table I

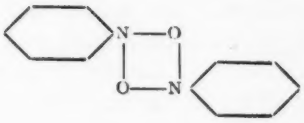
Absorption Maxima of Nitroso Compounds

Nitroso compound	Absorption maxima (Å)	Colour in solution in alcohol
Nitrosobenzene	7300	Green
p-Nitrosotoluene	7300	Green
Nitrosomesitylene	7320	Dark green
Ter-nitrosobutane	6390	Blue
Ter-nitrosoisopropylacetone ..	6600	Dark greenish blue

On account of the high strain in the molecule, most of the nitroso compounds tend to lose their internal strain by formation of more or less stable bi- or trimolecular compounds. Thus the colourless and comparatively more stable nitrosobenzene in benzene solution is found to be bimolecular,

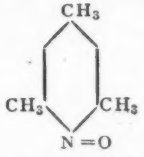
although in the vapour state it is intensely green, very unstable and monomolecular :

Nitrosobenzene
(Vapour ; intense green)

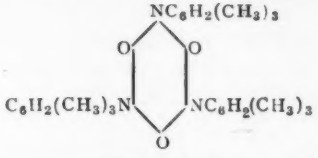


Nitrosobenzene
(Benzene solution ; colourless)

Similarly the unstable nitrosomesitylene in alcohol solution and also in the vapour state is emerald green and monomolecular, but in benzene solution and also in the solid state it is colourless, perfectly stable and trimolecular :



Nitrosomesitylene
(In alcohol ; emerald green)

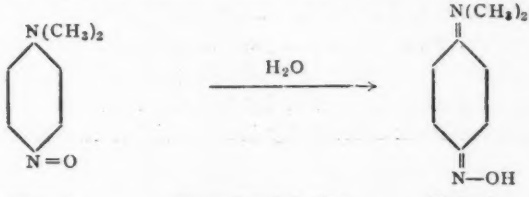


Nitrosomesitylene
(In benzene ; colourless)

The internal strain of nitroso compounds is also lost by formation of isonitroso compounds whenever there is a possibility of isomerism by the migration of a hydrogen atom in vicinity, as in the cases of nitroso-phenols or nitroso-naphthols, which are generally only yellow in colour :

Nitrosophenol — Quinoneoxime

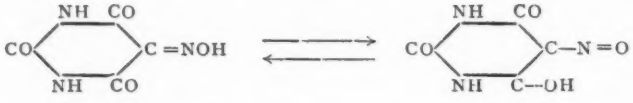
Similar change also takes place by the action of water on nitrosodialkyl anilines. Thus nitroso-dimethyl aniline is dark green in colour in the solid state, but in aqueous solution it is only yellow in colour :



(Green) — Nitrosodimethylaniline — (Yellow)

In many cases however there is a definite existence of resonance or tautomerism between the nitroso-enolic and the oximino-ketonic forms with a possibility of covalent links with chelate ring formations in the metallic derivatives such as in the cases of violuric acid and its various substituted derivatives and also in some of the isonitrosoisooxazolones studied by Dutt and his pupils, but all the interesting colour phenomena exhibited by these compounds can also be explained from the point of view of the theory of colour advanced by Dutt. This will be clear from the following explanations :

On account of the tautomerism between the nitroso-enolic and oximino-ketonic forms, many of the nitroso compounds do not exhibit the deep colours that are theoretically expected of them due to the extremely brief period during which they remain in the truly nitroso form. Thus in the classical example of violuric acid studied by Ghatak and Dutt,[2] the tautomerism between the two forms can be shown as given below :



Violuric acid
(Oximino-ketonic form ; colourless)

Violuric acid
(Nitroso-enolic form ; pink)

On account of this tautomerism, we find that violuric acid is colourless in the solid state and also in solution in non-hydroxylic solvents, and only pale pink in aqueous solution. But under special circumstances, that is, by the influence of organic or inorganic bases, the tautomerism between the two forms is arrested and the comparatively more acidic nitroso-enolic form is stabilised by salt formation. Consequently under such circumstances the deep colours that are expected of true nitroso compounds are developed. Thus we find that although violuric acid is colourless in the solid state and only very pale pink in aqueous solution, yet its salts with organic and inorganic bases are all crimson in colour, the intensity of the crimson coloration being roughly proportional to the strength of the basic character of the base undergoing salt formation. Exactly similar behaviour was noticed in the case of diphenyl-violuric acid by Prakash and Dutt,[3] of thio-violuric acid by Lal and Dutt,[4] of diphenylthio-violuric acid and its higher homologues and analogues by Dharam Dass and Dutt,[5] of isonitroso-malonyl-guanidine by Dharam Dass and Dutt,[6] of violantin and alloxantin by Gaind and Dutt[7] and of some derivatives of isonitroso-isooxazolones by Dutt and Dharam Dass,[8] as given in Table II.

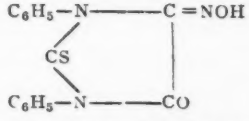
TABLE II

Colour of Isonitroso Compounds and their Salts

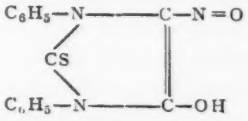
Name of the isonitroso compound	Colour of the substance	Colour of the salt
1 : 3-Diphenyl-violuric acid ..	Colourless	Purple
Thiovioluric acid	Light yellow	Purple
1 : 3-Diphenylthio-violuric acid ..	Light orange	Blue-green
Violantin	Colourless	Violet
Alloxantin	Colourless	Violet
Isonitroso-malonyl-guanidine ..	Light pink	Purple
Isonitroso-3-methyl-isooxazolone ..	Colourless	Crimson
Isonitroso-3-phenyl-isooxazolone ..	Colourless	Reddish-violet

In all the above instances, the transformation of the colourless or weakly coloured isomer into the strongly coloured compound is produced by the addition of organic or inorganic bases, when in order to effect the neutralisation of the base the weakly acidic oximino-ketonic forms are converted into the strongly acidic nitroso-enolic forms, with consequent great intensification of colour due to the stabilisation of a true nitroso group in the molecular structure, and the more or less complete stoppage of resonance between the oximino-ketonic and nitroso-enolic forms.

In the present investigation, isonitroso-1 : 3-diphenyl-thiohydantoin, which has been prepared for the first time by the action of nitrous acid on 1 : 3-diphenyl-thiohydantoin which has the oximinoketonic configuration shown below, has been found to undergo similar type of transformation by the action of organic and inorganic bases with production of a nitroso-enolic structure, and consequent great intensification of colour. Thus :



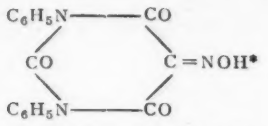
Isonitroso-1 : 3-diphenylthiohydantoin
(Oximino-ketonic form ; yellow)



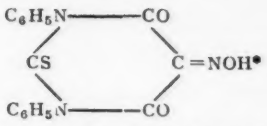
Isonitroso-1 : 3-diphenyl-thiohydantoin
(Nitroso-enolic form ; crimson)

Isonitroso-1 : 3-diphenyl-thiohydantoin is bright yellow in the solid state and in solution in organic solvents (non-hydroxylic), but on the addition of alkali or organic bases, an intense crimson coloration is formed, recalling the behaviour of violuric acid. In hydroxylic solvents like alcohol and acetic acid, a pinkish-yellow coloration is formed, and in this respect also it is similar to violuric acid. The salts of the compound obtained with organic and inorganic bases are perfectly stable at the ordinary temperature, and in most of the cases are precipitated in a beautifully crystalline condition when an alcoholic solution of the substance is mixed with an alcoholic or aqueous solution of the base. Salts with the following bases have been obtained : potassium hydroxide, sodium hydroxide, ammonium hydroxide, methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, iso-butylamine, pyridine, piperidine, and nicotine. For the sake of abbreviation, the properties of these substances together with their absorption maxima have been given in Tables III and IV. As in the case of compounds described by previous workers, it has also been found in the case of the present substance, that in general the stronger basic character of the base undergoing salt formation, the greater is the intensity of the colour of the salt thus produced. Many of the salts formed, in the solid state are almost colourless or have only pale colours, but in solution in aqueous alcohol, the deep colours that are expected from their molecular configurations are more or less fully developed. With very weak bases like aniline or dimethylaniline, isonitroso-diphenylthiohydantoin does not produce any stable salt formation, and consequently in presence of these bases no intensification of colour occurs.

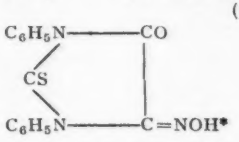
Compared to isonitroso-diphenylbarbituric acid (Prakash and Dutt[3]) and isonitroso-diphenylthio-barbituric acid (Lharam Dass and Dutt[5]), the intensification of colour of isonitroso-diphenylthio-hydantoin on salt formation is less pronounced, apparently due to the fact that in the first two compounds there are two CO groups in each of the molecules, capable of effecting the conversion of the isonitroso group into a true nitroso group by the transference of the labile hydrogen atom (marked with an asterisk), whereas in the third compound, there is only one such group existing. Consequently the possibility of formation of a true nitroso group with its concomitant intensification of colour is much greater in the first two cases than in the third. This is the reason why we find that the first two compounds form violet and green salts respectively, whereas the third form only crimson salts, although the molecular structures of all the three are closely analogous to one another. The idea will be quite clear by a look at the diagrams given below :



(IX) Isonitroso-diphenylbarbituric acid (Violet salts)



(X) Isonitrosodiphenylthio-barbituric acid (Green salts)



(XI) Isonitroso-diphenylthio-hydantoin (Crimson salts)

Experimental

*Preparation of isonitroso-*1 : 3-*diphenylthio-hydantoin.*—The 1 : 3-diphenylthio-hydantoin required for this purpose was prepared by the action of thiocarbanilide on monochloroacetic acid in an yield of about 64 per cent. in accordance with the method described by Lange.[9] 20 grams of the substance dissolved in 250 c.c. of glacial acetic acid were treated with 60 grams of finely powdered sodium nitrite in six equal instalments with vigorous stirring, each instalment being added at the end of every 24 hours and the reaction mixture allowed to stand at the ordinary temperature during the intervals between the additions. At the end of a week, the reaction product was poured into a large excess of water, and the precipitated orange-yellow sticky substance separated from the aqueous mother-liquor by decantation. On allowing it to stand in contact with water for about 48 hours, the sticky material completely solidified to an orange-yellow crystalline mass (24·6 gm.), which was filtered off, washed with water, dried and extracted with xylene which removed a small quantity of a dark yellow, viscous, uncrystallisable material. The residue (21·8 gm.) after complete removal of the xylene by aeration, was fractionally crystallised a number of times from alcohol of decreasing concentration into three main fractions, namely :

Fraction 1.—A bright yellow substance (1·2 gm.) crystallising in small rhombohedra, melting at 245° C. This was found to be free from sulphur and on account of the small quantity available, its identity could not be established.

Fraction 2.—A pale cream-coloured substance (6·3 gm.) crystallising in fine prismatic needles melting at 176° C. and giving no coloration with alcoholic ammonia. This was identified to be unchanged 1 : 3-diphenylthio-hydantoin.

Fraction 3.—A bright yellow substance (11·6 gm.) crystallising in glistening rectangular prisms, melting sharp at 174° C., and giving an intense

crimson colour with alcoholic ammonia. This was identified to be isonitroso-diphenylthio-hydantoin.

Isonitroso-1 : 3-diphenylthio-hydantoin crystallises from 40 per cent. alcohol in bright yellow glistening rectangular prisms, and from ether or benzene, in long feathery needles, with silky lustre, and melting at 174° C. in either form. It is easily soluble in alcohol, acetone, ether, chloroform, benzene and glacial acetic acid, moderately soluble in toluene, xylene, carbon tetrachloride and petroleum ether and insoluble in water. The solutions of the substance in organic solvents are bright yellow, but on the addition of alkali or strong organic bases, crimson colours are developed which become slightly intensified by the addition of a trace of water.

*Salts of isonitroso-*1 : 3-*diphenylthio-hydantoin.*—These were prepared by taking the hydantoin in alcoholic solution and adding slightly more than the equimolecular proportion of the organic or inorganic base, also in alcoholic solution. In most of the cases the salt crystallised out spontaneously from the solution in a fine state, but in some of the cases the solution had to be evaporated very quickly to dryness with the aid of a blast from a table fan, and the resulting crystalline salt washed with a little dry ether in order to remove any excess of the base.

The salts thus formed are exceedingly fine crystalline substances which are easily soluble in most of the organic solvents with the exception of ether and petroleum ether in which they are very sparingly soluble. In water they are only slightly soluble, but in contact with that solvent, they undergo very rapid hydrolytic decomposition partially with regeneration of isonitroso-diphenylthio-hydantoin, and partly with formation of complex bye-products. The properties of isonitroso-1 : 3-diphenylthio-hydantoin and its salts are given in Table III.

Summary and Conclusion

1. Isonitroso-1 : 3-diphenylthio-hydantoin has been obtained for the first time by the action of nitrous acid on 1 : 3-diphenylthio-hydantoin.

2. Isonitroso-diphenylthio-hydantoin has a bright yellow colour in the solid state or in solution in organic solvents, but on treatment with alkalies or organic bases, intense crimson coloured salts are formed the transition of colour from yellow to crimson being sufficiently strong and sharp for the compound to act as an excellent indicator.

3. The change of colour of the above compound from yellow to crimson has been shown from theoretical considerations to be due to a fundamental

TABLE III

Properties of Isonitroso-1 : 3-Diphenylthio-Hydantoin and its Organic and Inorganic Salts

Salt with	Colour in the solid state	Remarks	Colour in aqueous solution	M.P. (°C.)	Absorption maxima (Å)	Analysis (% S. theoretical values in brackets)
Methylamine ..	Brownish pink	Rectangular plates ..	Dark crimson	129	5540	9·56 (9·75)
Dimethylamine ..	Bright pink	Rectangular plates and prisms	,,	148	5520	9·31 (9·36)
Trimethylamine ..	Light buff	Long feathery needles ..	,,	152	5480	8·81 (8·98)
Ethylamine ..	Yellowish pink	Rectangular plates ..	,,	156	5520	9·22 (9·36)
Diethylamine ..	Bright pink	Long rectangular prisms	Crimson	179	5430	8·59 (8·65)
Triethylamine ..	Dark red	Rhombic prisms	Red	87	5270	8·15 (8·04)
Isobutylamine ..	,,	Prismatic needles	,,	167	5320	8·43 (8·65)
Pyridine ..	Light yellow	Glistening cubes ..	Orange	139	4550	8·29 (8·51)
Piperidine ..	Brownish pink	Long rectangular prisms	Dark crimson	158	5550	8·25 (8·37)
Nicotine ..	Pinkish brown	Rectangular plates ..	Red	132	5250	7·61 (6·98)
Potassium ..	Brownish pink	Glistening cubes ..	Dark crimson	167	5600	8·96 (8·55)
Sodium ..	Creamy yellow	Thin prismatic needles	,,	188	5550	10·51 (10·10)
Ammonium ..	Bright yellow	Glistening cubes	,,	112	5550	10·33 (10·20)
Free acid ..	,,	Rectangular prisms ..	Yellow	174	4435	10·65 (10·77)

TABLE IV

Comparison of the Absorption Maxima of the Salts of Isonitroso-diphenyl-barbituric acid, Isonitroso-diphenylthio-barbituric acid and Isonitroso-diphenylthio-hydantoin

Figures indicate Wave-lengths in Angstrom Units

Salt of	With Isonitroso-diphenyl-barbituric acid	With Isonitroso-diphenylthio-barbituric acid	With Isonitroso-diphenylthio-hydantoin
Methylamine ..	5810	6010	5540
Dimethylamine ..	5805	6030	5520
Trimethylamine ..	5765	6015	5480
Ethylamine ..	5785	6050	5520
Diethylamine ..	5875	6070	5430
Isobutylamine ..	5870	6000	5320
Pyridine	5825	5980	4550
Piperidine	5670	6140	5550
Nicotine	5650	..	5250
Sodium	5835	6610	5550
Potassium	5840	5660	5600
Ammonium ..	5845	6060	5550

change in the constitution of the molecules from an oximinoketonic to a nitroso-enolic form.

4. The above change is quite in accordance with a " Theory of colour on the basis of molecular strain," advanced by Dutt.

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A RAPID VOLUMETRIC METHOD FOR ESTIMATION OF IRON AND TITANIUM AND ITS APPLICATION TO ILMENITE ANALYSIS

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Received December 27, 1939

During recent years the production of ilmenite has increased steadily owing to the progress of the titanium oxide paint industry. Several scores of samples of the mineral had to be analysed by us in rapid succession in these laboratories and difficulties were experienced in the course of the work as the standard methods given in chemical literature were tedious and inconvenient.

The well-known colorimetric method for titanium which has been fully investigated by Hillebrand (1895), Walton, Jr. (1907), Faber (1907), Merwin (1909) and Wells (1911) can be usefully employed only when small amounts of titanium are present.

The gravimetric methods for estimation of titanium involve several precautions especially when iron also is present. Gooch (1885), Barnaby and Isham (1910), Thornton (1914), Lundell and Knowles (1919) and Hillebrand (1919) and others have devised various procedures, but all of them call for careful control of several factors and are therefore inconvenient.

Several volumetric methods for estimation of titanium have been suggested from time to time, the more important of them being due to the following investigators: Pisani (1864) Knecht and Hibbert (1903), Knecht (1905), Gallo (1907), Newton (1908), Eva Hibbert (1909), Shimer and Shimer (1912), Newmann and Murphy (1913), Ball and Smith (1914), Lundell and Knowles (1923), Takeno (1934), Thornton and Roseman (1935) and Hope Morgan and Ploetz (1936). The methods suggested by the above-mentioned workers utilise simple methods of reduction of the titanium followed by an oxidimetric titration with permanganate, ferric alum or other reagents. These will be referred to later in this paper.

The procedure for volumetric estimation of iron in presence of titanium usually consists in reduction with hydrogen sulphide and subsequent titration with permanganate. The method has been very carefully studied by Wells and Mitchell (1895), Coppadoro (1901), Washington (1904), McBride and Scherer (1917), Hillebrand (1919) and Lundell and Knowles (1921). All

workers lay stress on the importance of observing several precautions if accurate results are desired and these will be referred to in detail, later in this paper.

Experimental

Preparation of Solutions and their Standardisation.—0·1 N solution of potassium permanganate was prepared in the usual way and was accurately standardised by titration with pure sodium oxalate.

Approximately 0·05 N solution of ferric ammonium sulphate was prepared by weighing out the calculated amount of ferrous ammonium sulphate of known purity (99·51 %) dissolving it in water containing a small quantity of sulphuric acid and then oxidising it completely by heating with the minimum quantity of nitric acid. The solution was boiled to free it from oxides of nitrogen and then made up to volume after cooling. This solution was standardised by different methods as described below.

Titanium solution containing approximately 4 mg. per c.c. was prepared by fusing several portions of 5 g. of carefully purified TiO_2 with pure potassium bisulphate in hard glass test-tubes and dissolving the melt in dilute sulphuric acid and diluting the solution to the required volume. A saturated solution of potassium thiocyanate was employed in the titration of titanous salt with standard ferric salt solution.

Reduction of solutions was carried out in a Jones reductor which was of the usual size and contained a column of zinc about 35 cm. long resting on glass beads and glass wool. To prevent oxidation, the flask for receiving the reduced solutions was provided with inlet and outlet tubes for carbon dioxide.

The standardisation of the ferric salt solution was carried out by titration with standard permanganate after the solution had been reduced by either (*a*) hydrogen sulphide or (*b*) zinc in the reductor, observing the necessary precautions. Six experiments by each of the two methods gave the mean values 4·153 and 4·159 respectively, the general mean of all the experiments being 4·156 mg. Fe_2O_3 per c.c. of the ferric salt solution.

The titanium solution was standardised by the following methods: In one set of experiements, 25 c.c. portions of the titanium solution were reduced in the Jone's reductor and the reduced solution collected in an excess of ferric salt solution, a supply of carbon dioxide to the receiving flask being maintained throughout the experiment. The solution in the receiving flask was then immediately titrated with standard permanganate. It is well known that this procedure yields accurate results (Shimer and Shimer, 1912), owing to

the fact that titanous salt which is very unstable gets oxidised immediately by the ferric salt present, yielding an exactly equivalent amount of the relatively stable ferrous ion which can be titrated with better results. The titanium solution was also standardised after reduction, by titrating it with standard ferric solution, employing potassium thiocyanate as internal indicator. This titration had to be carried out quickly as otherwise low values were obtained owing to the rapid oxidation on exposure to air. A modification of this procedure which we devised was to keep in the vessel receiving the reduced solution, almost the required quantity of standard ferric solution as was known from the preliminary titrations. Usually 0·2–0·3 c.c. less than the quantity required was delivered from the burette into the receiving flask in which the reduced solution was to be collected, the reduced solution was then collected in it and the titration completed by cautious addition of ferric solution from the same burette after adding a small quantity of thiocyanate solution. We obtained very consistent results by this procedure and this involved no inconvenience or extra time.

The titanium solution was also standardised gravimetrically by precipitation with (*a*) ammonium hydroxide and (*b*) with sulphur dioxide. Six determinations were made by each of the two methods. The results obtained were in good concordance but the mean value obtained gravimetrically was higher by 0·18% than that obtained from the volumetric estimations.

Estimation of Iron in presence of Titanium.—One of the oldest methods for the estimation of iron in presence of titanium consists in passing hydrogen sulphide into the solution containing the two metals whereby only the iron is reduced while the titanium remains unaffected, thereby enabling the determination of the ferrous iron by titration with standard permanganate. The method is somewhat tedious and yields erratic results unless several conditions are strictly adhered to.

We carried out several experiments under varying conditions to investigate the reliability of the hydrogen sulphide reduction method for estimating iron, both in the presence and in the absence of titanium, the procedure being as follows : 25 c.c. of standard ferric solution was taken either by itself or along with 25 c.c. of standard titanium solution as required and diluted with water to about 200 c.c. Known quantities of sulphuric acid ranging from 2 to 20 c.c. were added, the solution heated almost to boiling and a steady current of purified hydrogen sulphide was passed for periods ranging from 1 to 3 hours. The current of hydrogen sulphide was maintained until the solution cooled to room temperature after which a current of purified

carbon dioxide was led into the solution which was gradually heated up to the boiling point. The heating was stopped as soon as the escaping vapours gave no test for hydrogen sulphide, and the solution was allowed to cool, the current of carbon dioxide being maintained throughout. The cooled solution was then titrated with standard permanganate solution. The results obtained are given in Table I, each value being the mean of at least six different experiments. The figures under col. A refer to the experiments where the solutions contained only iron and those under col. B to the solutions containing both iron and titanium. The results given in Table I show clearly that satisfactory results can be obtained by this method whether in the presence or in the absence of titanium, only if the acid concentration is maintained below about 3%.

TABLE I

Estimation of Iron by Reductions with H_2S

Concentration of	Period	$KMnO_4$ required	
H_2SO_4 %	hrs.	A c.c.	B c.c.
2·0	1	13·02	13·00
3·1	1	13·00	13·02
4·0	1	12·95	12·94
5·0	1	12·90	12·90
5·0	3	12·80	12·85
10·2	1	12·45	12·60
10·2	3	12·32	12·40

The volumetric estimation of iron by reduction of the solution with zinc and subsequent titration with standard permanganate was modified in the following manner, when titanium was also present in the solution. Since titanium is quantitatively reduced to the tervalent state in the reductor, while iron is being quantitatively reduced to the bivalent condition, treatment of the reduced solution with permanganate will yield a titration value corresponding to the sum of iron and titanium present. Since, however, titanous salts undergo rapid oxidation in air before titration is completed, it is necessary to collect the reduced solution from the reductor in an excess of ferric salt solution and thereby generate an equivalent amount of ferrous iron which

can be titrated with better results as it is relatively stable. Therefore, under the conditions of this experiment, the permanganate consumption represents the iron originally present in the solution as well as a quantity of iron exactly equivalent to the titanium present. The iron content of the original solution can therefore be calculated from this titration value by deducting the iron equivalent of the titanium which is determined by the method indicated below.

Estimation of Titanium in presence of Iron.—The most satisfactory procedure for the estimation of titanium whether in presence or absence of iron consists (as has been indicated earlier) in the reduction of the solution with zinc in the reductor and its subsequent titration with ferric salt solution. A useful modification which we devised was to collect the reduced solution in slightly less (0·2–0·5 c.c.) than the required quantity of ferric salt solution (as known from a preliminary experiment) and completing the titration in the usual manner, employing thiocyanate as indicator. We found that a sharp end point was obtained if 4 to 5 drops of the indicator were added and that it was unnecessary to use 5 c.c. of it as suggested by several workers.

Estimation of Titanium and Iron when both Metals are present.—The preliminary studies outlined above enabled us to adopt the following procedure for carrying out estimations of titanium and iron when both metals were present. 25 c.c. portions of standard iron solution were mixed with 25 c.c. portions of standard titanium solution, 10 c.c. of sulphuric acid (1 : 1) was added to the mixture which was then diluted to about 100 c.c. and used in each of the following experiments. The mixed solution was reduced in the reductor and titrated immediately with standard ferric solution and the quantity of ferric solution required was noted. Since this value was always low (as pointed out earlier) a fresh portion of the mixed solution was reduced in the reductor and the reduced solution caught in standard ferric solution (0·2–0·3 c.c. less than the quantity required in the previous experiment) and the titration completed as usual by further addition of standard ferric solution from the same burette. This modified procedure gave consistently accurate values for the titanium content of the solution, whereas the values calculated from the first experiement were too low as illustrated in the following example. In the first experiment, the mixed solution containing 25 c.c. of standard titanium solution (0·09820 g. TiO_2) required after reduction 23·45 c.c. of standard ferric solution, which corresponded to 0·09769 g. TiO_2. In the second set of experiments where 23·25 c.c. of standard ferric solution was kept in the receiving flask to collect the reduced solution and the titration completed with additions from the burette, the total quantity

required was 23·55 c.c. which corresponded to 0·09811 g. TiO_2 which is very close to the true value.

The estimation of iron in the solution containing both iron and titanium was carried out by titration with permanganate as follows. Since both iron and titanium are reduced quantitatively to the bivalent and tervalent stages respectively by zinc in the reductor, a titration of the reduced solution with permanganate will involve a permanganate consumption corresponding to the total of the iron and titanium present. As the quantity of titanium present (or its ferrous oxide equivalent) in the solution has been determined by previous titration with standard ferric solution, the corresponding permanganate consumption is also known. The quantity of permanganate required to oxidise only the ferrous iron is readily ascertained and the iron content of the solution calculated as usual. Since titanous solutions get readily oxidised in contact with air we adopted the procedure of collecting the reduced solution in an excess of ferric salt solution with the result that a quantity of ferrous iron exactly equivalent to the titanium was formed and which could be titrated with greater certainty. The calculation of results from the titration values may be illustrated by the following example:

(*a*) The mixture containing 25 c.c. of standard titanium solution (0·09820 g. TiO_2) and 25 c.c. of standard ferric sulphate solution (0·1038 g. Fe_2O_3) was passed through the reductor and found to require 23·57 c.c. of standard ferric solution. Since 1 c.c. of the standard ferric solution was known to correspond to 4·166 mg. of TiO_2, the TiO_2 content of the solution is found to be 0·0982 g.

(*b*) The mixture containing 25 c.c. of standard titanium solution and 25 c.c. of standard ferric solution was passed through the reductor and found on titration to require 25·30 c.c. of standard permanganate. Since we know from (*a*) that 0·0982 g. of TiO_2 is present and as this would on reduction consume 12·30 c.c. of the same permanganate, we find by subtraction that 13·00 c.c. of permanganate are consumed entirely by the ferrous iron formed from the iron in the solution originally taken for the analysis. Since 1 c.c. of the permanganate solution (0·1001 N) corresponds to 0·007995 g. of Fe_2O_3, we find that the iron content of the solution is 0·1040 g. of Fe_2O_3.

The true values of the iron and titanium contents of the solution taken for analysis are 0·09820g. TiO_2 and 0·1038g. Fe_2O_3 from which it can be seen that the experimental values are accurate. A final series of experiments was conducted with rigorous precautions which included the taking of varying quantities with a weight-burette. The results obtained are given below in Table II. The limits of accuracy obtainable with this method are also given in the table.

TABLE II

Analysis of Mixtures of Iron and Titanium

Quantities taken		Quantities found		Error per cent.	
Fe_2O_3 g.	TiO_2 g.	Fe_2O_3 g.	TiO_2 g.	Fe_2O_3	TiO_2
0·0714	0·1246	0·0712	0·1248	−0·27	+0·16
0·0840	0·1108	0·0842	0·1108	+0·25	−0·0
0·0914	0·1012	0·0916	0·1008	+0·22	−0·40
0·0972	0·0988	0·0970	0·0984	−0·21	−0·40
0·1002	0·0890	0·1002	0·0892	0·0	+0·22
0·1014	0·0816	0·1010	0·0816	−0·37	0·0
0·1102	0·0727	0·1104	0·0724	+0·19	−0·43

It can be seen from the above table that the maximum error in any determination is about 0·4 %, indicating thereby that the procedure adopted is reliable and sufficiently accurate.

Analysis of Ilmenite

Solutions required and their Standardization.—An approximately 0·1 N solution of potassium permanganate accurately standardised with sodium oxalate. An approximately 0·05 N solution of ferric sulphate is prepared by weighing out the calculated amount of ferrous ammonium sulphate, dissolving the salt in water containing some sulphuric acid, oxidising by warming with a small quantity of nitric acid and making it up to the required volume. 25 c.c. of this solution should give a permanent pink coloration with one drop of 0·1 N potassium permanganate solution.

The ferric solution is standardised by passing 25 c.c. of it through a Jones reductor and titrating the reduced solution with standard permanganate. From this titration, the Fe_2O_3 value per c.c. of the ferric solution is easily obtained.

The ferric sulphate solution should also be standardised with a solution of known titanium content. The solution of known titanium content is

reduced in the reductor and titrated with the ferric sulphate solution employing thiocyanate as indicator and observing the precautions mentioned earlier in this paper. From this titration we get the direct value per c.c. of the ferric solution in terms of TiO_2. In our experiments we found that the TiO_2 value as obtained by this titration agreed closely with the value calculated from the strength of the ferric solution with reference to permanganate.

The results of standardisation of the solutions employed for this work are given below:

1. The strength of the $KMnO_4$ solution was found to be 0·1001 N from which we get by calculation that 1 c.c. of it corresponds to 0·007995 g. of Fe_2O_3 or 0·007990 g. of TiO_2.

2. (*a*) 25 c.c. of the ferric sulphate solution required after reduction 13·00 c.c. of $KMnO_4$ (0·1001 N). Since 1 c.c. of the $KMnO_4$ solution corresponds to 0·007995 g. Fe_2O_3 (1), we find that the ferric solution has an Fe_2O_3 content of 0·004154 g. per c.c. From this it can also be found that 1 c.c. of the ferric solution will be equivalent to 0·004154 g. of TiO_2. (*b*) 25 c.c. of titanium solution containing 0·0982 g. TiO_2 required after reduction 23·57 c.c. of ferric sulphate solution. Therefore 1 c.c. of the ferric solution represents 0·004166 g. of TiO_2, and this value is in fair agreement with the value calculated in 2 (*a*).

3. 25 c.c. of titanium solution (0·0982 g. TiO_2) required after reduction 12·30 c.c. of $KMnO_4$ (0·1001 N). Hence 1 c.c. of $KMnO_4$ corresponds to 0·007984 g. TiO_2 and this is in good agreement with the value 0·007990 obtained directly by calculation from the strength of the permanganate solution 2 (*a*).

Analysis of Ilmenite.—1–1·5 g. of the finely crushed sample is fused in a hard glass test-tube with 10–12 g. of potassium bisulphate until decomposition is complete. The fused mass is then digested with sulphuric acid (1 : 4) until extraction of soluble matter is complete. The silica which separates may be filtered off, ignited and weighed if required. Otherwise no filtration is necessary and the entire acid extract may be transferred to a 500 c.c. volumetric flask and diluted with water up to the mark. The concentration of sulphuric acid in the solution could range from 10–15 % without detriment to ease of operation or accuracy of results. 50 c.c. portions of the solution from the volumetric flask are withdrawn for estimations of titanium and 100 c.c. portions for estimations of iron and the determinations carried out by the methods already described in the paper. The calculation of the results of analysis of a sample of ilmenite is illustrated below by an example.

1·2050 g. of ilmenite was fused and brought into solution and made up to 500 c.c.

(*a*) 50 c.c. of the solution was reduced in the Jones reductor and it was found to require 15·55 c.c. of standard ferric sulphate solution. Since this value is always rather low, the experiment was repeated with the modification that the reduced solution was caught in 15·30 c.c. of the standard ferric solution kept in the receiving flask of the reductor, and the titration completed by additions of ferric solution from the burette. The quantity of ferric solution consumed was 15·62 c.c.

Since we know that 1 c.c. of the ferric solution corresponds to 0·004166 g. of TiO_2, it follows that the TiO_2 in the sample is

$$\frac{15{\cdot}62 \times 10 \times 0{\cdot}004166 \times 100}{1{\cdot}2050} = 54{\cdot}01\,\%\ TiO_2.$$

(*b*) 100 c.c. of the solution was reduced in the reductor and the reduced solution collected in 50 c.c. of ferric sulphate solution. On titration this required 24·30 c.c. of $KMnO_4$.

We know from (*a*) that 100 c.c. of this solution contains 0·1301 g. of TiO_2, and this would after reduction consume 16·30 c.c. of $KMnO_4$, because 1 c.c. of $KMnO_4$ corresponds to 0·007984 g. TiO_2. Hence 24·30—16·30 c.c., *viz.*, 8·00 c.c. of permanganate corresponds to the quantity of iron present. Since 1 c.c. of the permanganate corresponded to 0·007995 g. of Fe_2O_3, the iron content of the specimen is

$$\frac{8 \times 5 \times 0{\cdot}007995 \times 100}{1{\cdot}2050} = 26{\cdot}55\,\%\ Fe_2O_3.$$

Since it would be incorrect to express all the iron present in the mineral as Fe_2O_3 or as FeO unless a separate estimation of FeO present in the sample is carried out, it would be advisable to express the iron content in terms of the metal when the result is expressed as Fe = 18·55 %.

In conclusion, we might report that several samples of ilmenite have been analysed by the above procedure both by us and by several other workers in these laboratories with satisfactory results.

Summary

1. A rapid volumetric procedure has been devised for the estimation of iron and titanium by titration with solutions of (*a*) ferric sulphate and (*b*) potassium permanganate.

2. The application of the above method to the analysis of ilmenite is described.

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A CHEMICAL AND MINERALOGICAL STUDY OF THE FELDSPARS FROM THE MICA-PEGMATITES OF NELLORE, MADRAS

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Introduction

The feldspars from the Nellore mica-pegmatites comprise different types varying in chemical composition and mineralogical properties.[1] The most abundant of these feldspars are (1) an albite-oligoclase containing about 10 per cent. of Na_2O along with 2 per cent. of K_2O and (2) an orthoclase containing 16 per cent. of K_2O and 0·5 per cent. of Na_2O. In addition to these two main types there are also found appreciable quantities of perthites the most conspicuous of them being a green orthoclase variety, and a flesh-red microcline feldspar. The green variety occurs with varying intensities of colour. Examination of such specimens revealed that their soda feldspar contents were variable and ranged from 22 to 30 per cent.

Of the feldspars noted above, those which occurred in considerable quantities were (1) albite-oligoclase, (2) white orthoclase, (3) flesh-red microcline and (4) green perthite-microperthite. The other feldspars, especially the cream-coloured variety and the microperthites are of limited occurrence and large lumps of these are seldom found.

The occurrence of mica in the pegmatite masses is a matter of great economic importance. It was noticed that workable deposits of mica were located only in such areas where there was a preponderance of the albite-oligoclase and orthoclase varieties and that in localities where the other varieties of feldspar preponderated the deposits were poorly developed.

Edmondson Spencer [2, 3, 4] has carried out an elaborate study of several varieties of potash-soda-feldspars, especially the perthitic ones, from various parts of the world. He has made detailed investigations on the moonstones (orthoclase-microperthites) and other related potash-soda-feldspars from Ceylon and various other localities and has discussed the relationship between their chemical and physical properties and also the effect of high temperatures upon them. He has analysed some specimens of microcline-microperthites

and an albite from the mica-pegmatites of Kodarma, Bihar, and also a few specimens of microcline-microperthites from Patna State, Orissa. Finally, in his last paper, he has applied the results of his earlier investigations to some questions of petrogenesis and differentiation with particular reference to granite and granite pegmatites. Spencer's work, excepting that on the moonstones from Ceylon, is of a general character dealing with the chemistry of the microperthites in relation to their physical properties and origin.

While dealing with the composition of granite pegmatites Spencer[5] makes a remark on the Kodarma pegmatites. He says, " Quantitatively, the Kodarma pegmatites are predominantly potassic, the majority being of the ' simple' quartz-microcline-muscovite type. Where the soda feldspar is present in more than subordinate amounts, it occurs almost to the exclusion of the potash feldspar. There is nothing approaching the 40 : 60 potash : soda-feldspar ratio of Vogt's residual magma".

Recently Sharma[6] has published a detailed megascopic and microscopic study of the feldspars from the mica-pegmatites of Kodarma. But he has not given any chemical analysis of these feldspars. A perusal of the paper gives no idea of the proportions of soda and potash feldspars in the pegmatite mass, but it is apparent that potash feldspar predominates.

It is rather interesting to note that while the feldspars from the Kodarma pegmatites have received widespread attention those from the Nellore pegmatites have received very little attention. In spite of their large distribution these feldspars have not been studied systematically. Sometime back Biswas[7] published a paper discussing the probable origin of the mica-pegmatites of Nellore, but he made no detailed reference to the individual feldspars present therein. His reference to the feldspars is as follows: " The pegmatite magma constitutes a system of albite-orthoclase-muscovite-quartz-volatiles equilibrium. The prevalence of sodic plagioclase (andesine to albite) in pegmatite dykes of Nellore indicates a melt initially saturated with these compounds. The relation between the potash feldspar and these sodic plagioclases is a eutectic one with extensive zones of solid solutions on either side of the boundary curve."

The feldspars from the mica-pegamatites of Nellore form an interesting series and unlike those of Kodarma they are made up of a mixture of the soda and potash varieties in equal proportions. Sometimes the sodic variety preponderates over the potassic one and thus approaches the 40 : 60 potash : soda-feldspar ratio of Vogt's residual magma. Nowhere in the Nellore pegmatites is the soda feldspar found to occur to the complete exclusion of the potash feldspar. The sodic variety of the Nellore feldspar is an albite-oligo-

clase-muscovite-quartz-type, the potassic variety being an orthoclase-muscovite-quartz type. These feldspars also differ from those of the Kodarma pegmatites in that the main potassic variety is orthoclase instead of microcline. The present work was undertaken to study in detail the above characteristics of the feldspars from the Nellore pegmatites.

Megascopic and Microscopic Characters

The feldspars studied in this work can be classified under three main heads as follows: (*a*) Feldspars without perthitic intergrowths (*non-perthitic*), *viz.*, Albite-oligoclase, orthoclase and microcline; (*b*) Perthite-microperthites; and (*c*) Microperthites.

Non-perthitic Feldspars: (*a*) *Albite-Oligoclase.*—This feldspar is widely distributed and is almost always white with the characteristic twinning striations on (001) face. It comprises two or three different types with a slight variation in composition. Most of the samples examined were quite fresh and they showed only a slight alteration when examined under the microscope. Several specimens revealed the presence of scattered inclusions of muscovite scales. Some samples of this feldspar exhibit a parallel growth with clear glassy quartz, and some of them are characterised by a subdued play of colours. This phenomenon is visible only when the crystals are held in a particular angle to the incident light. Sections cut parallel to (001) show between crossed nicols the characteristic albite lamellar twinning. Extinction angle on (001) with reference to the trace of (010) cleavage is symmetrical, 2° 30′ and 3°. Extinction angle on (010) with reference to the trace of (001) cleavage is 16° and 15° 30′.

Two samples of the feldspar from two different areas, one from the Thallabedu Mica Mine and the other from the Shaw Mica Mine, were analysed and their compositions are given in Table II. A recalculation of the two analyses in terms of various feldspar molecules results in the following formulæ: (1) $Or_{12}Ab_{85}An_3$ and (2) $Or_9Ab_{87}An_4$.

(*b*) *White Orthoclase.*—This feldspar also occurs over a large area and is snow-white in colour. Though specimens from the surface show considerable alteration, the alteration is only very slight in samples from the fresh rock. Such alteration can be seen along cracks where there is a turbidity due to the formation of kaolin. Excepting for a few small grains of quartz as well as of minute scales of muscovite, this feldspar is very pure. It is closely associated with clear quartz and also with big books of muscovite mica. It presents clevages in two directions, *viz.*, parallel to (001) and (010), the former one being better developed than the latter. It shows no twinning and only in one case was a very faint incipient microcline twinning noticeable. Extinction

angle on (001) with reference to (010) = 4° 30′. Extinction angle on (010) with reference to (001) = 6°.

A sample of this feldspar was subjected to chemical analysis (No. 3, Table II) and the composition calculated as feldspar molecules gives the following formula : $Or_{96\cdot7}Ab_3An_{0\cdot3}$. In addition to this specimen, two other specimens of orthoclase, one from Pallimitta Mica Mine and the other from Shaw Mine, were also analysed, but they were found to contain more soda and less potash than the specimen mentioned above. Microscopic examination of these two latter specimens showed the presence of thin veins of albite, thus confirming the results of chemical analysis. Very faint cross-hatching, not of the microcline but of the green perthite type, was also noticed in these two feldspars.

Swaminathan[8] examined several specimens of feldspars and has published the results of their chemical analysis. Although the specimens examined by him and by the author were from the same locality, the author has found serious variation in the chemical composition of the feldspars and he considers that Swaminathan's results require revision.

(*c*) *Flesh-red Microcline.*—Though hand specimens of this feldspar appear fresh, they reveal under the microscope an advanced state of alteration and turbidity. The kaolinization of this feldspar is more pronounced in (001) and (100) sections than in (010) sections. Isolated inclusions of albite which are not in optical continuity with the microcline host are found scattered without any definite orientation. No perthitic inclusions either of the films or veins type were noticeable. The cross-hatch is rather coarse (Microphotograph, Fig. 1, Pl. V). The cleavage parallel to (001) is alone well developed. Under high power this feldspar shows fine vesicles of ferruginous matter distributed unevenly throughout its body. Extinction angle on (001) with reference to the trace of (010) = 15° 20′. Extinction angle on (010) with reference to the trace of (001) = 5° 40′.

A sample of this feldspar was analysed and the results obtained were expressed in feldspar molecules. The formula was found to be $Or_{93\cdot9}Ab_{5\cdot6}An_{0\cdot5}$.

Perthite-Microperthites.—This group includes the following four types of feldspars :

(*a*) rich green orthoclase perthite
(*b*) pale-green orthoclase perthite
(*c*) pearl-white orthoclase perthite and
(*d*) flesh-red microcline perthite.

The last two of these four feldspars are only of very limited occurrence.

The Green Perthite-Microperthite.—This variety has been observed previously by Swamianthan and is described by him in his paper.[9] This feldspar is not of restricted occurrence, as in addition to the localities mentioned by Swaminathan, it is also often met with in many of the test pits in Saidapuram, where search was made for good muscovite mica. It is also found in the waste heaps from a few abandoned mica pits.

This feldspar is unique in character and offers many interesting points for study. The potash member of this feldspar appears to be an orthoclase, and is green in colour. It shows the presence of very fine cross-hatching on (001) face, but sections or cleavage flakes parallel to this face give almost straight extinction with reference to the trace of (010) cleavage. The coarse albite lamellæ or 'veins' extend regularly in a direction almost parallel to (100). The veins vary in size and shape. In sections cut parallel to (001) they range in width from 0·2 mm. to 1·2 mm. while on (010) sections, the range is from 0·5 mm. to 1·2 mm. The (010) sections show regular alternate bands of albite and potash feldspar along a direction which makes an angle of about 70° with the trace of the basal cleavage. This angle, however, is found to be variable. In addition to these wide perthitic bands, one can also notice microperthitic lamellæ of albite, which owing to their higher birefringence than the surrounding potash feldspar could be observed between cross nicols under the microscope. With (001) sections these microperthitic bands of albite lie almost parallel to the wide albite bands, *i.e.*, parallel to the edge *ac* and normal to the trace of (010). In addition, one could see in the (001) sections, very minute microperthitic bands of albite, much smaller than those mentioned already. When seen through crossed nicols they appear as very faint and narrow lighted areas. These lamellæ lie also in a direction parallel to the general run of perthitic bands but in a few cases they are also found lying in a perpendicular direction.

In all the perthitic feldspars analysed, it was found that the perthitic bands, whether of the 'vein' type or the 'film' type, were almost always longer in sections cut parallel to (001) than in sections cut parallel to (010). The thickness of these films is less in (010) sections than in (001) sections. The length of the coarse perthitic lamellæ varies from 1″ to 3″ in (001) sections and from ·5″ to 2″ in (010) sections. In (010) sections of these feldspars, the perthitic and microperthitic structures are more regular and uniform than in (001) sections. Under low magnification, extinction angle for (010) with reference to (001) cleavage is found to be about 7°. Under high magnification, however, there is considerable separation of the microperthitic lamellæ of albite, which permits accurate measurement of the extinction angles of the two feldspars. The extinction angle of the potash feldspar

is about 5° and that for the soda feldspar of the microperthites about 20°. Under high magnification, the microperthitic structure is better defined on (010) sections than on (001) sections. In (010) sections the films (microperthitic lamellæ) are packed very closely. They appear to be shorter and thinner than those found on (001) sections (Microphotographs, Figs. 2, 3, 4 and 5, Pl. V). Multiple albite twinning is seldom observed in the microperthitic lamellæ.

The ' primary' or ' vein' perthite is very common in these green perthites and their lamellæ exhibit in almost all cases on basal sections the characteristic albite multiple twinning. Because of the very fine cross-hatching exhibited by the potash member of these feldspars and the fact that the ' vein' type of perthitic bands which are commonly met with only in microclines are present in these feldspars also, these have so far been wrongly considered to be microcline perthites.

The presence of cross-hatching in the potash member of this feldspar is interesting, because it exhibits the optical properties of an orthoclase and not microcline. (001) Cleavage flakes of this feldspar show almost straight extinction with reference to the trace of (010) cleavage while microcline would give an extinction angle of 15° 30′. Secondly, sections cut parallel to (010) show almost symmetrical interference figures in convergent polarized light. The obtuse bisectrix which is the direction of slow vibration is almost normal to (010) and parallel to the crystallographic axis *b*, while in microcline the obtuse bisectrix would make an angle of 15° 30′ with the normal to (010). Calculation of the optic axial angle from the refractive indices (Table I) gives about 50° while for microcline it is 83°. These observations show that the green potash feldspar is not microcline, but a feldspar of the orthoclase type.

The soda feldspar occurring as perthitic bands is white and so appears prominently on the green background of potash feldspar. The perthitic structure is easily seen with the naked eye, because the perthitic bands or ' veins ' are rather coarse and have a thickness of about 1 mm. The microperthitic structure, however, is so fine and composed of such extremely thin elongated bands of albite oriented almost parallel to the coarse albite bands that a high magnification is necessary for their examination. On (001) sections, the coarse 'primary' or ' vein ' perthitic bands show occasionally along their width the pinching-in and swelling out effect which is commonly observed in the albite bands of perthite.

(001) *Cleavage Flakes.*—Extinction with reference to the trace (010) is straight for the potash member, at times reaching 1° to 1° 30′. Extinction for the albite-oligoclase bands is symmetrical and the angle of extinction is

4°. The extinction angle shown by the microperthitic lamellæ of albite is difficult to measure, but it is less than 3°. Cloudy patches mixed with fine granular matter are observed under high power in the body of the potash feldspar. The cloudy turbid patches which do not appear to be due to kaolinization, show a very faint birefringence. The feldspar is hidden from view in those places where these turbid patches occur. The plagioclase feldspar is free from these cloudy patches. The cross-hatching in the potash feldspar is very fine and uniform under low power and the lines of the cross-hatching are very closely packed. But under high power this cross-hatching is found to be made up of very fine alternating dark and white lines which present a fibrous structure (Microphotograph, Fig. 1, Pl. VI). The spacing of these lines is not uniform and they traverse alternating, longitudinal and horizontal zones of dark and bright areas (Microphotograph, Fig. 2, Pl. VI). These alternating bands of dark and light areas run parallel to the direction of general run of the perthitic lamellæ and also perpendicular to this direction. This effect is due to the close and regular packing of the dark fibrous bundles of the cross-hatching, which enclose bright areas in which these fibrous bundles are more widely spaced. Thus this type of longitudinal and horizontal bright and dark zones results in a 'mat'-like structure and the resulting cross-hatching looks as if it is made up of alternating bright and dark squares (Microphotograph Fig. 3, Pl. VI). The alternating bright and dark bands running parallel to the direction of the perthitic and microperthitic lamellæ are developed more prominently than those running perpendicular to this direction. The contacts between the coarse albite bands and the potash feldspar are always slightly irregular and form a serrated border which becomes noticeable only when the section is examined between crossed nicols. There is invariably present in the potash member at its junction with the soda member a thin zone which does not generally show an uniform extinction, nor is it extinguished simultaneously with either of the feldspars. The extinction angle of this zone of feldspar is about 10° with reference to the trace of (010) cleavage.

(010) *Cleavage Flakes.*—Extinction of the potash member with reference to the trace of (001) cleavage is oblique and the extinction angle for the bright green and pearl-white feldspars is 5° 20′ while for the pale green feldspar it is slightly more, *viz.*, 6°. Short, sinuous and spindle-shaped microperthitic lamellæ are found in abundance parallel to the usual perthitic plane and form an angle of 70° 30′ with the trace of basal cleavage. The extinction angle of these microperthitic lamellæ is slightly more than that of the coarse perthitic bands and it is 20° with reference to the basal cleavage. The extinction angle of the coarse perthitic bands of albite is 19°. These sections give a

biaxial symmetrical interference figure for the potash member when examined between crossed nicols in convergent polarized light.

Sections perpendicular to (010) *and almost parallel to* (100).—In these sections the traces of the basal cleavage and the (010) cleavage cut each other at 90°. When examined between crossed nicols in convergent polarized light these sections give a biaxial interference figure which is almost symmetrical.

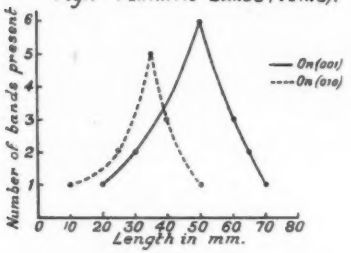
An examination of the two sections (010) and (100) shows that the optic axial plane is perpendicular to (010) and only slightly inclined to the basal plane. The Bx_o, which is the direction of slow vibration, is almost normal to (010) and parallel to the crystallographic axis *b*. The Bx_a, which is the direction of fast vibration, makes an angle of + 5° 20′ with the crystallographic axis *a*.

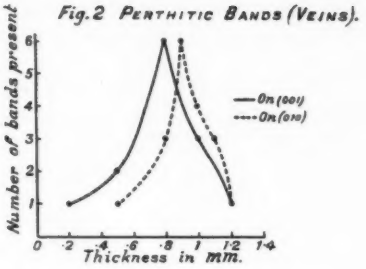
Size and Distribution of the Perthitic and Microperthitic Lamellæ.—The bands of albite in these feldspars can be classified into two main groups :—(i) The coarse perthitic bands or 'veins' which vary from 0·2 mm. to 1·2 mm. in thickness and from 20 mm. to 80 mm. in length.

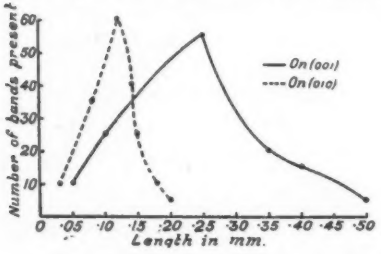
(ii) (*a*) Fine microperthitic lamellæ ' films' varying from 0·001 mm. to 0·005 mm. in thickness and from 0·05 mm. to 0·5 mm. in length. These lamellæ form the main feature of the microperthites and they can be compared to the ' strings' mentioned by Alling[10] in his recent paper on plutonic perthites.

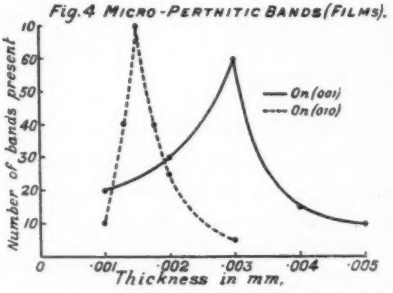
(*b*) Very fine lamellæ, not so abundant as those of the previous type. They can be compared with the ' stringlets' of Alling.[10] Unlike the ' strings' and ' stringlets' of the plutonic perthites examined by Alling the zones of these microperthitic lamellæ not only overlap but also intergrade. They are not distinct in size and distribution. The transition from one type to the other is very gradual and imperceptible. For the sake of convenience, however, these microperthitic lamellæ are subdivided into two classes according to Alling to indicate their approximate size.

Curves showing the size of perthitic and microperthitic lamellæ as well as their distribution in (001) and (010) sections of the green feldspar are given in Figs. 1–4.









The Pearl -White Perthite-Microperthite.—Despite the lack of colour this variety resembles in all other properties the green perthite. It is similar to the green perthite which has been deprived of its colour by heat treatment. This feldspar exhibits schiller phenomenon to a marked degree.

Flesh-red Microcline Perthite.—This feldspar has only a very limited distribution and occurs as small isolated patches within the flesh-red microcline belt. The potash member, which is a typical microcline, has coarse cross-hatching on (001). It resembles more or less the flesh-red microcline described already. Only one set of cleavages parallel to (001) alone is well developed. This feldspar is considerably altered.

Microperthites.—These are seldom found in large lumps and are observed only in the mica dumps but not in the pegmatite dykes. A detailed examination of these feldspars was not undertaken due to want of sufficient material. But chemical analyses of small specimens were carried out to ascertain their relation to the major feldspars of the pegmatite. Microscopic examination reveals that they resemble the microperthitic portion of the perthite-microperthites, but they differ in the distribution and size of the microperthitic lamellæ. The microperthitic lamellæ, which are larger in size and more numerous than those in the green perthites, are closely packed together.

These microperthites can be classified into four groups according to their colour: (i) Green microperthite, (ii) Pale-green microperthite, (iii) Cream coloured to white microperthite, and (iv) Flesh-red microcline microperthite. The optical properties of the first three groups resemble closely those of the microperthitic portion of the green perthite. The extinction angle on (001) with reference to the trace of (010) varies from 0° to 2° and on (010) with reference to the trace of (001) it varies from 6° to 7°. Due to the close packing of the microperthitic lamellæ it is difficult to measure accurately the extinction angles. The flesh-red microcline microperthite shows an extinction angle of about 15° on (001) and about 6° 30′ on (010).

Specific Gravities and Refractive Indices.—Specific gravities, refractive indices, optic axial angles and birefringence (calculated from the refractive indices), and the extinction angles of the various samples are given in Table I.

TABLE I

Specimen	Sp. Gr.	Refractive indices			Calculated optic axial angles (2V.)	Birefringence (γ–α)	Extinction angles	
		α	β	γ			*On* (001)	*On* (010)
1	2·6158	1·5256	1·5297	1·5358	78·9°	·0102	2° 30′	16°
2	2·6209	1·5254	1·5292	1·5357	73·2°	·0103	3°	15° 30′
3	2·5608	1·5188	1·5250	1·5266	58°	·0078	1° 30′	6°
4	2·5655	1·5207	1·5251	1·5278	78·5°	·0071	15° 20′	5° 40′
5	2·5765	..	..	..	..	..	..	..
6	2·5668	1·5198	1·5242	1·5250	49°	·0052	0°–1° 30′	5° 20′
7	Not determd.	..	..	..	..	..	1°	19°
8	2·5781	*1·5199	1·5244	1·5253	52·2°	·0054	0°–1°30′	5° 20′
9	2·5809	..	..	..	..	..	..	..
10	2·5704	1·5200	1·5243	1·5256	60°	·0056	0°–2°	6°
11	2·5836	*1·5210	1·5255	1·5283	70·5°	·0073	15°	5° 30′
12	2·5722	1·5197	1·5236	1·5247	55·2°	·0050	0°–1′	6° 30′
13	2·5730	1·5202	1·5246	1·5255	48·2°	·0053	0°–1° 45′	6° 54′
14	2·5742	1·5205	1·5247	1·5261	64°	·0056	1°20′	6° 49′
15	2·5691	1·5214	1·5243	1·5277	85·1°	·0063	13° 52′	6° 32′

* Determination of refractive indices, etc., were made for the *Or* microperthitic portion only.

The determination of refractive indices was made with an Abbe refractometer using thin polished slices cut parallel to the principal planes of the indicatrix. The good development of the (010) face, which forms one such plane, facilitates easy working of this method. Further, this method was found to be better suited for the determination of refractive indices of these feldspars than the well-known immersion method. The correction is only about $\pm$ ·0002. But this method has only a limited application as it requires initial fixing up of the principal planes of the indicatrix and as such unsuited for the determination of the refractive indices of irregular grains.

The specific gravities of the powdered samples were determined by the specific gravity bottle method as recommended by Tutton.[11]

Specimens taken for examination.—

Nonperthitic	1.	White albite-oligoclase ..	from Thallabedu
	2.	White albite-oligoclase ..	from Shaw Mine
	3.	White orthoclase ..	from Thallabedu
	4.	Flesh-red microcline ..	from Pallimitta
Perthite-microperthites	5.	Green perthite ..	from L. N. Mine
	6.	Green portion (potash feldspar) of No. 5	,,
	7.	White portion (albite) of No. 5	,,
	8.	Pearl-white perthite ..	from Thallabedu
	9.	Pale-green perthite ..	from L. N. Mine
	10.	Green portion (potash feldspar) of No. 9.	,,
	11.	Flesh-red microcline perthite ..	from Pallimitta
Microperthites	12.	Green microperthite ..	from L. N. Mine
	13.	Pale-green microperthite ..	,,
	14.	Cream coloured to white microperthite	from Pallimitta
	15.	Flesh-red microcline microperthite	,,

Preparation of Specimens for Chemical Analysis.—To separate prior to chemical examination the perthitic and microperthitic constituents of the specimens of feldspar, the following method proved helpful. Since the two constituents were present in layers of appreciable thickness and were also well separated, a simple process of careful grinding was sufficient to yield thin plates of each constituent uncontaminated with the other. The thin plates thus obtained were examined microscopically prior to their chemical analysis.

Method of Analysis.—Samples which had been examined and found to be free from surface impurities were crushed to fine powder, in an agate mortar.

A weighed quantity of the material (0·5 gm.) was fused with pure anhydrous sodium carbonate in a platinum crucible. The cooled melt was taken in dilute hydrochloric acid, and silica, alumina, calcium and magnesium were determined as usual. Iron was estimated colorimetrically by the well-known potassium thiocyanate method. For the estimation of alkalies a separate portion of the material was analysed by the Lawrence Smith method and the alkalies were weighed as chlorides. From these mixed chlorides potassium was determined by the cobaltinitrite method as modified by Wasselieef and Matwejeb[12] and perfected by Sunawala and Krishnaswami.[13] The amount of sodium chloride was obtained by difference and the corresponding Na_2O calculated.

TABLE II

Chemical Composition Per cent.

Specimen	SiO_2	Al_2O_3	Fe_2O_3*	MgO	CaO	Na_2O	K_2O	Loss on ignition	Total
1	67·19	20·20	0·08	Nil	0·61	9·85	2·10	0·16	100·19
2	67·25	20·35	0·05	Nil	0·72	10·15	1·59	0·14	100·25
3	64·27	18·70	0·07	0·02	0·05	0·36	16·05	0·20	99·72
4	64·32	18·95	0·31	0·02	0·09	0·64	15·49	0·30	100·12
5	65·15	19·19	0·22	0·01	0·14	2·50	13·02	0·20	100·43
6	64·71	18·42	0·28	0·02	0·05	1·12	15·05	0·22	99·87
7	66·99	20·28	0·12	Nil	0·60	9·55	2·45	0·14	100·13
8	64·89	19·15	0·09	0·01	0·16	2·44	13·10	0·18	100·02
9	65·47	19·31	0·15	0·02	0·17	3·51	11·52	0·20	100·35
10	64·85	19·00	0·22	0·02	0·07	1·84	13·99	0·21	100·20
11	65·34	19·10	0·34	0·01	0·10	3·03	12·23	0·33	100·48
12	64·83	18·82	0·27	0·02	0·08	1·70	14·09	0·16	99·97
13	65·08	18·95	0·14	0·01	0·10	1·95	13·83	0·22	100·28
14	64·82	19·01	0·10	0·02	0·13	2·12	13·52	0·21	99·93
15	64·71	18·85	0·31	0·01	0·08	1·56	14·36	0·30	100·18

* Total iron expressed as Fe_2O_3.

TABLE III

Percentage Mineral Composition of the Specimens

(Calculated from Table II)

Per cent.

	Feldspars				Other constituents				
	Potash feldspar	Soda feldspar	Anorthite	Total feldspar	Excess SiO_2	Excess Al_2O_3	Fe_2O_3	MgO	Loss (H_2O)
1	12·23	83·32	3·12	98·67	0·68	0·59	0·08	..	0·16
2	9·40	85·94	3·67	99·01	0·54	0·55	0·05	..	0·14
3	91·80	2·93	0·28	98·01	0·75	0·60	0·07	0·02	0·20
4	91·63	5·45	0·50	97·58	1·03	0·87	0·31	0·02	0·30
5	76·84	20·96	0·78	98·58	0·66	0·71	0·22	0·01	0·20
6	88·68	9·53	0·28	98·49	0·62	0·15	0·28	0·02	0·22
7	14·74	80·70	3·06	98·50	0·69	0·74	0·12	..	0·14
8	77·28	20·85	0·88	99·01	0·28	0·60	0·09	0·01	0·18
9	67·94	29·44	0·93	98·31	0·81	0·73	0·15	0·02	0·20
10	82·73	15·60	0·38	98·71	0·38	0·61	0·22	0·02	0·21
11	71·89	25·45	0·56	97·90	1·06	0·72	0·34	0·01	0·33
12	83·34	14·15	0·45	97·94	0·95	0·58	0·27	0·02	0·16
13	81·35	16·50	0·56	98·41	0·83	0·58	0·14	0·01	0·22
14	79·62	17·92	0·73	98·27	0·64	0·73	0·10	0·02	0·21
15	84·84	13·20	0·45	98·49	0·51	0·52	0·31	0·01	0·30

TABLE IV

The Quantities of the Feldspar Members Recalculated to a total of 100

Samples	$K_2O \cdot Al_2O_3 \cdot 6\ SiO_2$	$Na_2O \cdot Al_2O_3 \cdot 6\ SiO_2$	$CaO \cdot Al_2O_3 \cdot 2\ SiO_2$	$(Ab + An)$
	Or	*Ab*	*An*	
1	12·40	84·44	3·16	87·60
2	9·49	86·80	3·71	90·51
3	96·72	2·99	0·29	3·28
4	93·90	5·58	0·52	6·10
5	77·95	21·26	0·79	22·05
6	90·04	9·68	0·28	9·96
7	14·97	81·93	3·10	85·03
8	78·05	21·06	0·89	21·95
9	69·11	29·95	0·94	30·89
10	83·81	15·80	0·39	16·19
11	73·43	26·00	0·57	26·57
12	85·09	14·45	0·46	14·91
13	82·67	16·77	0·56	17·33
14	81·02	18·24	0·74	18·98
15	86·14	13·40	0·46	13·86

TABLE V

Quantities of the Two Feldspar Members as Calculated from Micrometric Measurements

Samples	*Or* mixed crystal by weight	*Ab* mixed crystal by weight	*Ab* by weight as microperthitic lamellæ in the *Or* mixed crystal
5	80·64	19·36	3·12
8	79·28	20·72	3·21
9	77·75	22·25	3·25
11	79·48	20·52	4·21
12	89·75	10·25	9·87
13	87·43	12·57	12·31
14	87·02	12·98	12·60
15	90·87	9·13	8·76

In Table VI (*a*) are given the micrometric measurements of specimens 5 and 9 (the green and pale-green perthite microperthites) and in Table VI (*b*) are given the mineral composition of these two feldspars with those of the Or and Ab mixcrystal components of specimen 5 and Or component of specimen 9, as calculated from their respective chemical composition. Results in Table VI (*c*) were derived by direct calculation from Tables VI (*a*) and VI (*b*). It was assumed, during this calculation, that the microperthitic albite is of the same chemical composition as that of the vein albite.

TABLE VI

Distribution of the Three Feldspar Members (Or, Ab and An) in Feldspars 5 *and* 9

Results obtained from the various methods	Feldspar member and its distribution	Specimens				
		5	6	7	9	10
(*a*) Calculated from micrometric measurements	*Or* mixcrystal by weight	80·64	..	..	77·75	..
	Ab mixcrystal by weight	19·36	..	..	22·25	..
	Ab mixcrystal in *Or* mixcrystal as films	3·12	..	..	3·25	..
(*b*) Calculated from chemical composition	Potash feldspar *Or* ..	77·95	90·04	14·97	69·11	83·81
	Soda feldspar *Ab* ..	21·26	9·68	81·93	29·95	15·80
	Anorthite *An* ..	0·79	0·28	3·10	0·94	0·39
	(*Ab* + *An*) ..	22·05	9·96	85·03	30·89	16·19

(*c*)		Specimen No. 5		Specimen No. 9
		Calculated from analysis No. 5		Calculated from analysis No. 9 with the help of analysis 10
		With the help of analysis 6	With the help of analysis 7	
Calculated from both (*a*) & (*b*) above	(i) *Or* in *Or* mixcrystal	75·41	75·52	67·89
	(ii) *Or* in *Ab* mixcrystal	2·54	2·43	1·22
(The quantities given here represent the percentage amount in the total specimen)	(iii) (*Ab* + *An*) in *Or* mixcrystal	8·40	8·75	12·80
	(iv) *Ab* in *Or* mixcrystal	8·11	8·44	12·49
	(v) *An* in *Or* mixcrystal	0·24	0·29	0·31
	(vi) *Ab* as solid solution in *Or*	4·99	5·32	9·55
	(vii) *An* in *Ab* of the *Or* mixcrystal	0·29	0·31	0·31
	(viii) (*Ab* + *An*) in *Ab* mixcrystal	13·65	13·30	18·09
	(ix) *Ab* in *Ab* mixcrystal	13·10	12·80	17·46
	(x) *An* in *Ab* mixcrystal	0·55	0·50	0·63

Discussion

Table IV shows that the albite-oligoclase feldspar (Nos. 1 and 2) contains 84·44–86·80 per cent. of soda feldspar and about 3 per cent. of anorthite. The orthoclase feldspar (No. 3) from Thallabedu mica mine holds about 97 per cent. of potash feldspar, the rest being soda feldspar whereas the flesh-red microcline (No. 4) from Pallimitta holds a slightly larger quantity of soda feldspar. In the perthite-microperthites (Nos. 5, 8, 9 and 11) the amount of potash feldspar varies from 69 per cent. to 78 per cent., soda feldspar from 21 to 30 per cent. and anorthite from 0·57 to 0·94 per cent. In the microperthites the percentage of potash feldspar ranges from 81 to 86 per cent., soda feldspar from 13 to 18 per cent. and anorthite from 0·46 to 0·74 per cent.

It can be seen from Table VI (*c*) that in the orthoclase mixed crystal (green portion) of the green perthite microperthite (No. 5), the amount of potash feldspar *Or* actually present is only about 75·5 per cent. of the total feldspars whereas the chemical analysis of the specimen 5 reveals the presence of nearly 78 per cent. of this constituent. It can therefore be deduced that about 2·5 per cent. of *Or* is present in the perthitic lamellæ of albite in a state of solid solution. This orthoclase mixed crystal also contains about 8 per cent. of soda feldspar partly (about 5 per cent.) in solid solution and partly (about 3 per cent.) as microperthitic lamellæ of albite. An examination of the pale-green perthite-microperthite (specimen 9) gives similar results excepting that this feldspar contains a larger percentage of soda.

It can be seen from Table VI (*c*) that in the albite mixed crystal (the coarse perthitic lamellæ or ' veins') of the green feldspar (specimen 5) the amount of soda feldspar *Ab* actually present is about 13 per cent. whereas chemical analysis of specimen 5 indicates the presence of this constituent to the extent of 21 per cent. These results show that 8 per cent. of soda feldspar is present in the *Or* mixed crystal. The amount of anorthite present in specimen 5 is very low being only 0·79 per cent. of which 0·5 per cent. occurs in the soda feldspar of the ' veins' (*Ab* mixed crystal), and the rest occurs in the *Or* mixed crystal, most probably along with the soda feldspar present therein.

The above points indicate that in these perthitic feldspars mutual solubility exists between the potash and soda members on the one hand, and the soda member and anorthite on the other, whereas the potash member and anorthite appear to be immiscible. It can be deduced therefore that the small amount of anorthite present in the *Or* mixed crystal is due to the presence of albite which can hold it in solution. This view is supported by the fact that the ratio of *Ab* to *An* is almost the same both in the *Or* mixed,

crystal and in the *Ab* mixed crystal. It also follows from this view that the pure potash member should be free from anorthite.

Heat-treatment.—Almost all the coloured feldspars, excepting the flesh-red and cream coloured ones, lose their colour on heating them even at 300° C. The rich green perthite loses its colour on heating and is changed into a pearl-white feldspar. The cloudy patches seen in thin sections of the green feldspar disappear on heating and are converted into opaque granular material. Heating the specimens of the various perthitic feldspars at a temperature of about 800° C. and subsequent slow cooling to the room temperature does not produce any change in the perthitic structure or in the cross-hatching of the potash member. But on continued heating in the vicinity of 1000° C. and cooling suddenly, the following changes become noticeable. Some of the microperthitic lamellæ disappear almost completely and are replaced by areas which show a slightly higher birefringence than the surrounding potash member. The coarse perthitic bands, however, retain their original characters on heating, but the contact zones between them and the orthoclase host appears slightly widened. The zone is no longer sharp but develops into a somewhat ill-defined area which is not extinguished simultaneously with either of the feldspar members. The extinction angle for this zone on (001) face with reference to the trace of (010) is about 10°. Under similar conditions of heat treatment the cross-hatching of the potash feldspar tends to fade out. The extinction angles of the soda and potash feldspars were not altered by heating, but that of the potash member on (010) section showed a slight increase.

The Relationship between Iron Content and Colour.—Though a glance at the composition of these feldspars does not give us any clue as to the exact role of iron, a closer study reveals that iron plays an important part in the colouration of these feldspars. The increase in the quantity of iron with the increase of colour is easily noticed, but the colour itself may differ. The flesh-red feldspars which contain the maximum amount of iron owe their colour to the potash feldspar (microcline) which contains numerous minute specks of ferruginous vesicles. These vesicles are distributed throughout the mass of the potash feldspar and are abundant especially near its contacts with the albite present in the microcline perthites. These vesicles are rarely present in the albite lamellæ. The colour of these flesh-red feldspars is not destroyed by heat. The ferruginous vesicles occur largely in isolated areas and because of this the colour is never uniform throughout. Even in the case of the cream coloured feldspar the colour is probably due to vesicles of ferruginous matter, although no proof of it could be obtained microscopically. The very pale

yellowish pink-colour of this feldspar is not destroyed by heat but persists like that of flesh-red feldspar even at high temperatures.

The green colour of the perthites and microperthites is completely destroyed by heat. The loss of colour is brought about even at a very low temperature, *viz.*, 300° C. and this loss of colour does not result in any noticeable change in the structure of the feldspar. But analyses carried out before and after heating show that almost all the iron present originally in the ferrous state is oxidised during heating.

The green colour of these feldspars is caused by a green turbidity probably due to a ferrous compound in a fine state of division as cloudy patches within the body of the feldspar. These special areas of turbidity were absent in the heated specimens. However, thick specimens of this mineral lose their general transparency on heating and become translucent and sometimes opaque acquiring a pearl-white colour. This is perhaps due to the development of numerous cracks within the feldspar. But such development of cracks in the body of the feldspar cannot explain loss of the original green colour, because small fragments which developed no cracks showed similar loss of green colour on heating. Thin sections of the heated specimens are perfectly clear except for the isolated patches of a granular opaque material in places originally occupied by the cloudy patches. The cloudy patches which are present in thin sections of the feldspar before heating render the whole field somewhat hazy but heating the specimen to 300° C. removes this turbidity (Microphotographs, Figs. 4 and 5, Pl. VI) and the sections show clearly all the minute details.

Though almost all the perthites examined exhibit schiller, the colour shown by them are not true schiller colours but due to a metallic impurity such as iron. The iron is present in the ferrous state in the green feldspar and as a ferric compound (probably as hematite or limonite) in the flesh-red feldspars. Although it appears that the schiller exhibited by these feldspars is due to their microperthitic structure, no relationship could be deduced between the nature of the microperthite structure and the colour of the specimens. Specimens with a poor development of the microperthitic structure exhibited feeble schiller effect and those with regular development of the microperthitic structure exhibited the effect strongly.

Origin of the Green Perthite-Microperthite.—Biswas[7] has discussed the origin of the Nellore mica-bearing pegmatites in a generalised manner. He has not, however, considered in detail the origin of the individual feldspar members of the pegmatite. It is generally considered that the two major

feldspar members, *viz.*, orthoclase (including microcline) and albite-oligoclase, are the direct products of crystallisation of the potash-rich and soda-rich portions respectively of the residual pegmatite magma. The origin of the perthites cannot however be explained by the above simple view. To discuss the origin of these perthites, especially the green variety, it is necessary to consider their close association with minerals such as samarskite and beryl. The concentration of such minerals found in the close vicinity of these feldspars suggests that these feldspars crystallised during the last stages of consolidation of the potash-rich portion of the pegmatite magma.

The perthitic bands, *viz.*, the veins and films, appear to have formed simultaneously with their potash feldspar host and bear an eutectic relation to it because :

(i) The ($Ab + An$) content of the coarse perthitic bands is uniform, *viz.*, 19 per cent. of the total feldspar.

(ii) Though the change from the ' film' to the ' vein' type is not gradual, several perthitic bands having intermediate sizes are often present.

(iii) Small lense-shaped blebs of albite are found scattered in the potash feldspar and these have a similar optical oritentation as that of the albite present in the ' veins'.

(iv) The contact zones of the *Or* with *Ab* are similar on either side of the vein.

(v) The abundance and size of the ' films' in the potash feldspar are the same near the veins as in regions further away.

(vi) The ' vein' as well as the ' film' perthite are in optical continuity with their orthoclase host.

Summary

The various feldspars from the mica-pegmatites of Nellore have been examined microscopically and chemically. They could be grouped under three main heads according to their composition and microscopic characters, *viz.*, (1) feldspars without any perthitic intergrowths, or non-perthitic variety, (2) perthite-microperthites and (3) micro-perthites.

These feldspars do not show on heating any appreciable alteration, excepting that in the green variety the colour is completely lost. The colour of the green feldspar can be attributed to the presence of a greenish turbidity due to a ferrous compound which gets oxidised on heating and loss of colour occurs.

The soda and potash members of the green perthites were separated by an easy method and they were examined chemically. The results of analysis

were utilised to calculate the composition of the perthite as regards the various feldspar members present therein. This procedure also yielded data regarding the mutual solubility of the various feldspar components present. It could be deduced that such mutual solubility exists, though to a limited extent, between the potash and soda feldspar on the one hand and between soda feldspar and anorthite on the other. Potash feldspar and anorthite, however, seem to be immiscible. It can be noticed that the soda member is more soluble in the potash member than *vice versa*.

It is shown that the colour of these feldspars is not schiller colour but due to an iron compound. The schiller exhibited by these feldspars appears to be due to their microperthitic structure.

The perthitic feldspars appear to have formed during the later stages of consolidation of the pegmatite magma. The ' vein' and the ' film' types of perthitic lamellæ seem to have originated simultaneously with their potash feldspar host.

Acknowledgment

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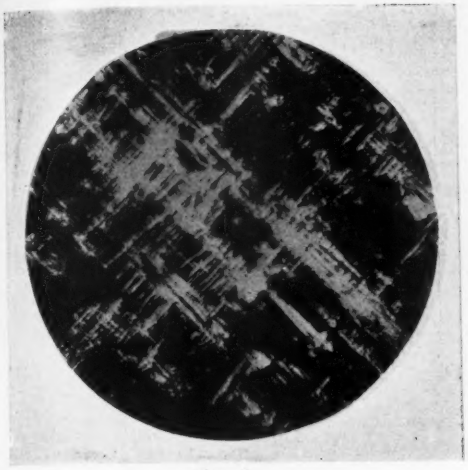
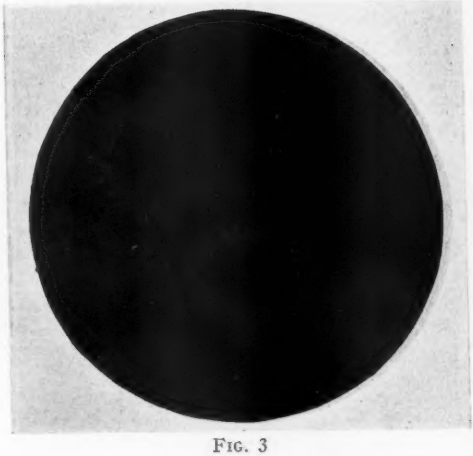


FIG. 1

FIG. 2



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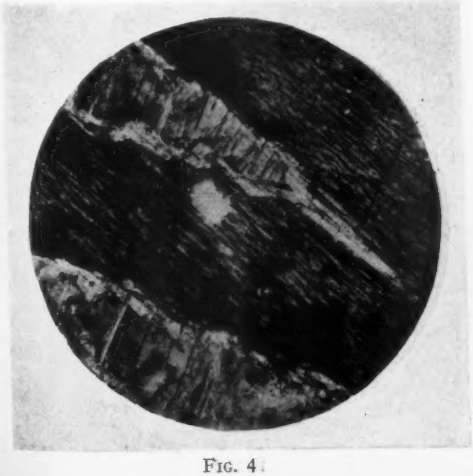

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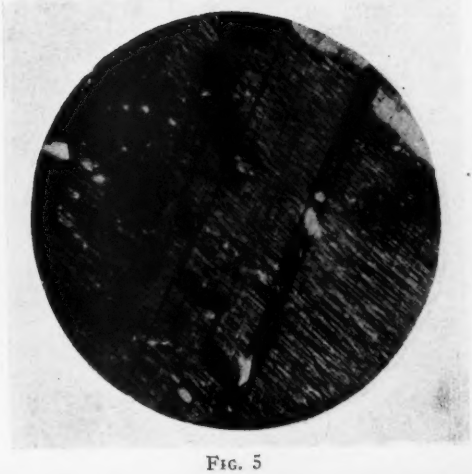


FIG. 5

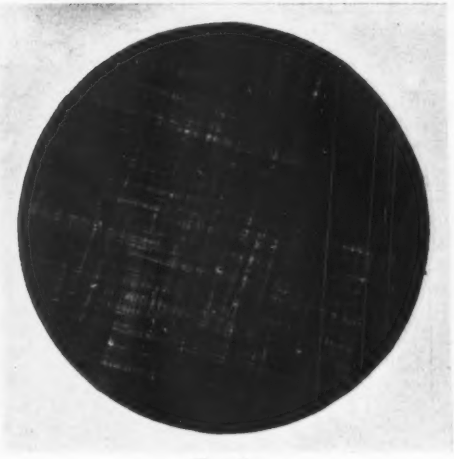


FIG. 1

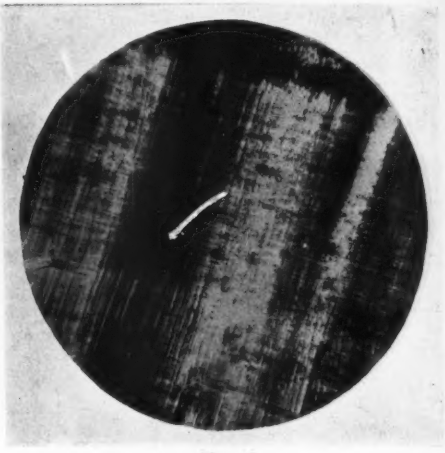
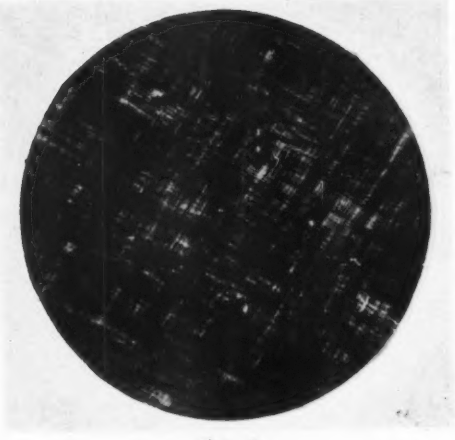


FIG. 2



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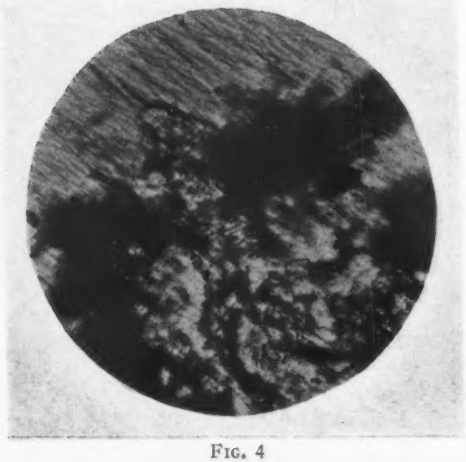

FIG. 4

FIG. 5

MICROPHOTOGRAPHS

PLATE V

FIG. 1.—The flesh-red microcline feldspar showing the characteristic microcline twinning. It shows the difference in the cross-hatching between this feldspar and the orthoclase portion of the green perthite (Plate VI, Fig. 1)—(001) section. × 30. Between + nicols, near the position of extinction.

FIG. 2.—The rich green perthite-microperthite area between two ' veins ' of albite showing the ' films ' or ' strings ' as fine thin white lines. (001) section × 40. Between + nicols.

FIG. 3.—The pale-green perthite-microperthite showing a ' vein ' and numerous ' films '. (001) section. × 40. Between + nicols.

FIG. 4.—The rich-green perthite-microperthite showing both the ' veins ' and ' films ' of albite. Traces of the basal cleavage are also visible. (010) section × 40. Between + nicols.

FIG. 5.—The pale-green perthite-microperthite showing both the ' veins ' and ' films ' of albite. Traces of the basal cleavage are prominently seen.—(010) section × 40. Between + nicols.

PLATE VI

FIG. 1.—The *Or* mixcrystal (green) portion of the green perthite-microperthite showing a fine cross-hatching. (001) section. × 60. Between + nicols.

FIG. 2.—The *Or* mixcrystal portion of the green feldspar highly magnified showing the alternate dark and white banding of the cross-hatching. (001) section, × 600. Between + nicols.

FIG. 3.—The ' mat '-like structure presented by the cross-hatching—(001) section. × 100. Between + nicols (very close to the position of extinction).

FIG. 4.—The cloudy patches of turbidity in the orthoclase mixcrystal portion of the green perthite-microperthite before heating—(001) section. × 200. Between parallel nicols.

FIG. 5.—The *Or* mixcrystal portion of the green perthite-microperthite after heating it to 300° C. The cloudy patches have disappeared leaving behind a fine granular matter—(001) section. × 200. Between parallel nicols.

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